Structure - property relationships in early transition metal based olefin polumerisation catalysts

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2 Titanium Complexes with Linked Cyclopentadienyl Amido Ligands*†

Titanium complexes of linked dianionic cyclopentadienyl-amide ancillary ligands (figure 2.1) are effective catalysts for the (co-)polymerisation of olefins when activated with the appropriate cocatalysts.[1,2] When compared to the metallocenes, these so-called "constrained geometry catalysts" (CGC's) are thermally more stable and generally produce polymers of higher molecular mass.[3] The increased electron deficiency and reduced steric encumbrance of these complexes relative to the well-known group 4 metallocene catalysts[4] make these systems of particular interest for fundamental studies on the effect of the ligand system, activator and electronic state of the metal on catalyst performance.

The linked cyclopentadienyl amido ligand system was introduced by Bercaw *et al.* in 1990 (A, figure 2.1) in organoscandium chemistry.[5] The steric environment of the resulting compounds is more open than the bis(pentamethylcyclopentadienyl)scandium system, studied earlier by the same group,[6] resulting in systems that are polymerise

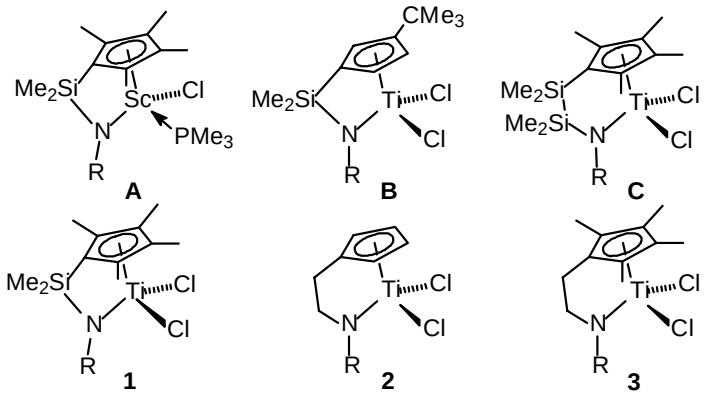

Figure 2.1. Constrained Geometry-type catalysts.

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* The syntheses of the tetramethylcyclopentadienyl ligands (**7a**–**c**), described in section 2.1.1 were developed by Daan van Leusen. The syntheses of the dialkyl species (**11**–**14**) and the determination of their polymerisation characteristics (section 2.1.4) have been performed by Maaike Wander.

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α-olefins, albeit on a slow rate. Soon after, Okuda *et al.* introduced the ligand on titanium (B, figure 2.1).[7] Several companies published patents in which cyclopentadienyl-amide titanium dichlorides and dialkyls, after treatment with MAO, are used as catalysts for the copolymerisation of ethene with higher olefins (1-hexene, and 1-octene),[1a–c,e,8,9] diolefins[10] and cyclic monomers such as norbornene.[11,12] The interesting catalytic properties of these systems prompted various research efforts to elucidate the effect of changes in catalyst structure on catalytic activity.[2]

It was observed early on that, in the cyclopentadienyl-amido Ti(IV) systems, the ligands with the tetramethyl-substituted cyclopentadienyl give catalysts that are superior in performance to those with the unsubstituted cyclopentadienyl moiety.[8d,2] In ethene/α-olefin copolymerisation with the titanium dichlorides and MAO cocatalyst, the combination of a $SiMe_2$-bridge with a ^{t}Bu amido substituent (**1a**) seems to give the best results in terms of productivity and comonomer incorporation.[8d] The ease of incorporation of comonomer drops when the $SiMe_2$-bridge is replaced for a $(CH_2)_2$- or a $(SiMe_2)_2$-bridge. For the $(CH_2)_2$-bridge the experiments suggest a higher productivity than for the $SiMe_2$-bridged analogue, whereas for the $(SiMe_2)_2$-bridged system the lower comonomer incorporation is accompanied by a decrease in activity.[8d] Reports on structure-activity relationships by Okuda *et al.* also show that there seems to be a synergy: for $[C_5Me_4(SiMe_2)NR]TiCl_2$ (**1**)/MAO an activity-trend in the order of R = ^{i}Pr < ^{t}Bu < CH_2Ph is observed, whereas the order in the case of the $[C_5Me_4(SiMe_2CH_2)NR]TiCl_2$/MAO is CH_2Ph < ^{i}Pr < ^{t}Bu.

In ethene and propene polymerisation with Cp-amide catalysts with usubstituted Cp-moiety ($[C_5H_4(CH_2)_2NR]TiCl_2$, **2**),[2] the molecular weight of the obtained polymers increases with decreasing size of R, opposite to the trend in activity, and also opposite to the trend observed with the $[C_5Me_4(SiMe_2)NR]^{2-}$ systems.[13,14] In these systems, a large effect of the cocatalyst is observed, when switching from the dichloride/MAO to dibenzyl/borane activation, resulting in significant changes in molecular weight and stereoselectivity of the resulting polymer. It was suggested that the increase in molecular weight could be tuned by choosing an appropriate complementary anion.[13]

Although there are many studies on cyclopentadienyl-amide systems, there are some issues regarding these catalysts that deserve closer investigation. The first subject is based on the observation that for $[C_5Me_4(bridge)N^tBu]TiCl_2$ (**1a**)/MAO the activity seems to increase by changing the bridge from $SiMe_2$ to $(CH_2)_2$, but that the latter shows a lower incorporation of α-olefins.[8d] A closer study of catalysts supported by the $[C_5Me_4(CH_2)_2NR]^{2-}$ ligand is presented in section 2.1.

Second is the observed effect of the activator on the polymerisation characteristics of catalysts of the type $[C_5H_4(CH_2)_2NR]TiX_2$ (X = Cl, **2**; CH_2Ph, **15**).[13] The observed changes in molecular weight and stereoregularity of the polymer depending on activator

provide a possible probe for the anion dependency of the selectivity of the catalyst.[13] These studies are presented in section 2.2.

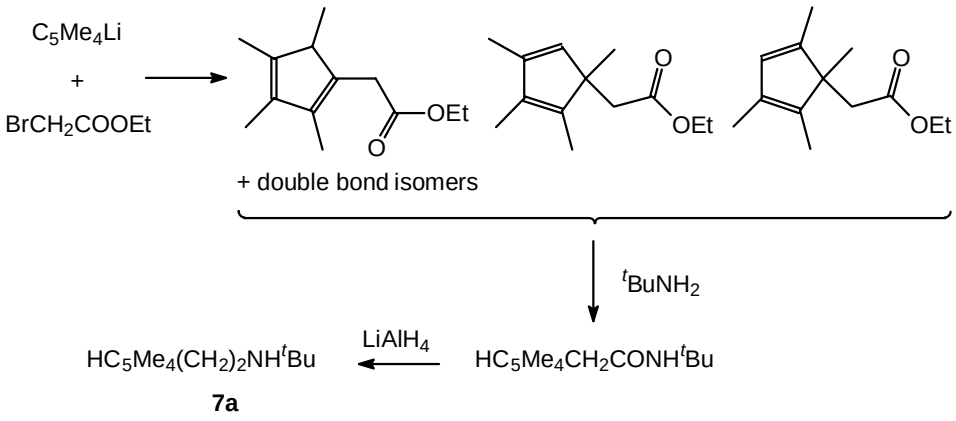
2.1 Ethylene bridged tetramethylcyclopentadienyl amido ligands

To separate the effects of the nature of the bridge and the substitution pattern of the cyclopentadienyl ligand, we set out to prepare a series of ethylene bridged tetramethylcyclopentadienyl-amide ligands $[C_5Me_4(CH_2)_2NR]^{2-}$ and their titanium dichloride derivatives **3** (R = ^{t}Bu, **3a**; ^{i}Pr, **3b**; Me, **3c**). The resulting systems are compared to the archetypal $[C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**1a**). Section 2.1.1 describes the synthesis approach to the ligand systems and sections 2.1.2 and 2.1.3 respectively describe catalyst synthesis and polymerisation activity.

2.1.1 Ligand synthesis

Synthesis of the amines of the type $HC_5Me_4(CH_2)_2NHR$ (**7**) is nontrivial for several reasons. In principle, tetramethylcyclopentadienide anion can be used as precursor, but the regioselectivity of the alkylation of tetramethylcyclopentadienide is generally poor (as the geminal substitution products usually dominate).[15] One of the targeted ligands, $HC_5Me_4(CH_2)_2NH^tBu$ (**7a**), was described in a patent as being synthesised (with unspecified yield) via this methodology (scheme 2.1).[8d]

An alternative route starts from dialkylamine derivatives $HC_5Me_4(CH_2)_2NR_2$. These are available through double *sec*-butenylation of the esters $R'O(O)C(CH_2)_2NR_2$, followed by dehydration and cyclisation.[15a] This diamine can be used as precursor to 4,5,6,7-tetramethylspiro[2,4]cyclohepta-4,6-diene[16] which, on reaction with various carbon, phosphorus or arsenic-centred nucleophiles can be converted to heteroatom substituted ligands.[17] Unfortunately this ring opening reaction is not observed for amides.[18]



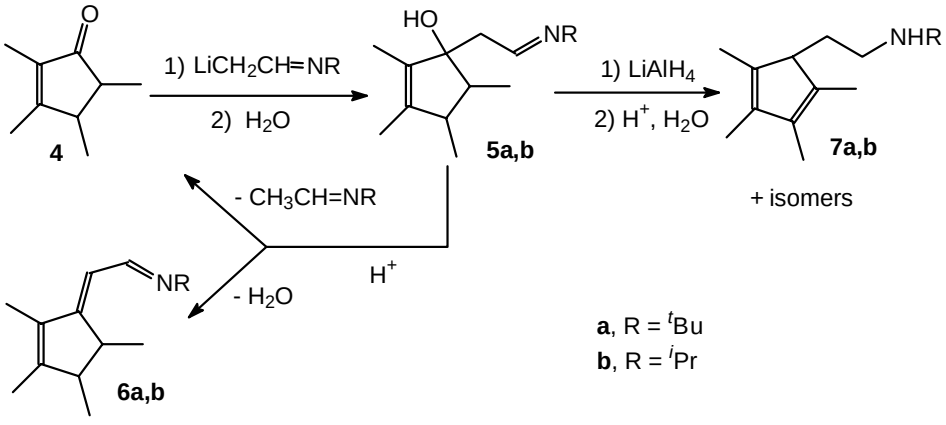
Scheme 2.1.

The use of 2,3,4,5-tetramethylcyclopent-2-enone (**4**) as precursor in a synthesis of these ligands (comparable to its use in the synthesis of C_5Me_5H)[19] is limited due to the instability of 2-heteroatom-functionalised alkylmagnesium or lithium compounds.[20] Nevertheless, this method can be used when an unsaturated functional group is introduced which can be converted to the desired amine functionality. In the following paragraphs we describe the use of 2,3,4,5-tetramethylcyclopent-2-enone (**4**) and N-alkylimines or nitriles as precursors for the synthesis of the desired amine ligands.

Synthesis of $HC_5Me_4(CH_2)_2NHR$ (R = ^{t}Bu, ^{i}Pr).

Acetaldehyde N-isopropylimine or acetaldehyde *N-tert*-butylimine was lithiated in THF at –20°C with the weakly nucleophilic base LiN^iPr_2 (generated *in situ* from ^{n}BuLi and diisopropylamine) and reacted with cyclopentenone **4** (scheme 2.3). Subsequent hydrolysis of the reaction mixture yielded the crude alcohols **5**. These intermediates are not very stable and decompose upon distillation, reforming the starting materials. Attempts to perform acid-catalysed dehydration of the alcohols also resulted in formation of the cyclopentenone **4** although the imines $C_4Me_4H_2C{=}CHCH{=}NR$ (**6a**, **6b**) could be obtained and spectroscopically characterised via this procedure. Fortunately, direct reduction of the crude alcoholates with $LiAlH_4$ in diethyl ether, followed by aqueous workup and an acid-base separation, yielded the desired cyclopentadiene products $HC_5Me_4(CH_2)_2NHR$ (R = ^{t}Bu, **7a**; R = ^{i}Pr, **7b**). The isolated yields, after vacuum destillation, are modest: 21% for **7a** and 39% for **7b** (based on cyclopentenone **4**). Especially for R = ^{t}Bu concomitant formation of a substantial amount of 1,2,3,4-tetramethylcyclopenta-1,3-diene is observed, probably due to the reversibility of the C,C-bond formation and subsequent reduction of the formed cyclopentenone **4**.

The various products were characterised by combinations of IR, ^{1}H and ^{13}C NMR



Scheme 2.2

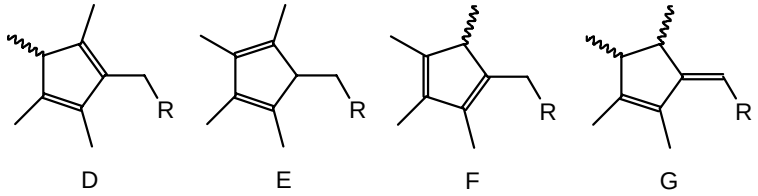


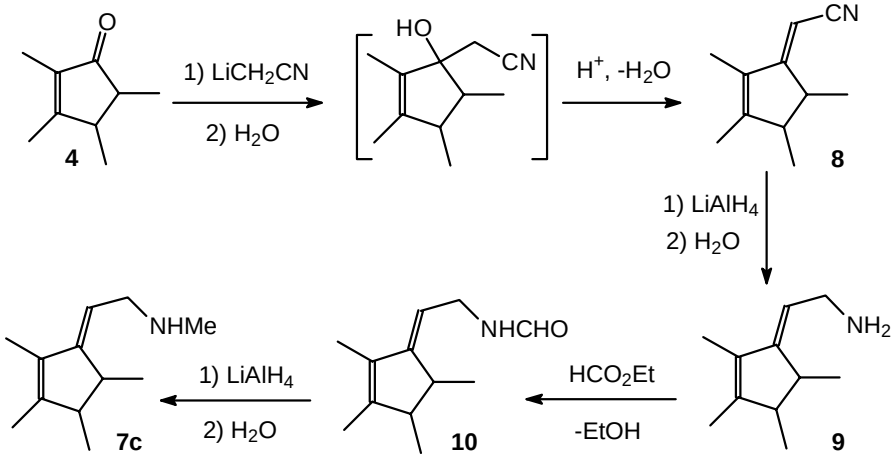
Figure 2.2. Endo- (D-F) and exocyclic (G) isomers.

spectroscopy and exact mass spectroscopy. The cyclopentadienyl-amines **7a** and **7b** consist of a mixture of the three endocyclic double bond isomers D – F as shown in figure 2.2.

Synthesis of $HC_5Me_4(CH_2)_2NHR$ (R = H, Me).

For the methylamino derivative $HC_5Me_4(CH_2)_2NHMe$ (**7c**) a different strategy is required, as the appropriate imine, acetaldehyde N-methylimine, is not sufficiently stable under basic conditions to be used as a reagent.[21] Deprotonated acetonitrile is therefore employed as nucleophile for the reaction with the cyclopentenone **4** (scheme 2.3). Dehydration and reduction yields the parent amine $HC_5Me_4(CH_2)_2NH_2$ (**9**) which was subsequently converted to the methylamine derivative (**7c**).

Reaction of lithiated acetonitrile with **4** in THF gave, after acidic work up and vacuum distillation, the [2,3,4,5-Tetramethyl-cyclopent-2-enylidene]-acetonitrile **8** in an almost quantitative yield (98%). Reduction of this nitrile with $LiAlH_4$ in diethyl ether, followed by hydrolysis and vacuum distillation yielded the amine $H_2C_5Me_4{=}CHCH_2NH_2$ (**9**, 70%). Formylation of the amine in refluxing ethylformate gave the crude N-formyl $H_2C_5Me_4{=}CHCH_2NHCHO$ (**10**). Subsequent reduction of **10**



Scheme 2.3.

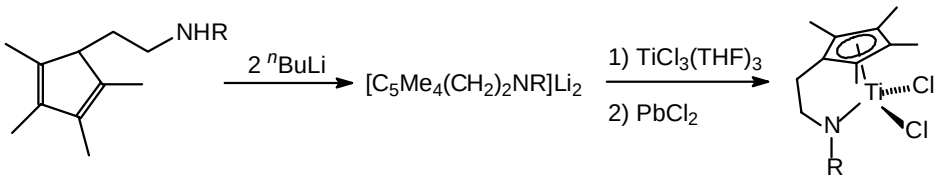
with $LiAlH_4$ in diethyl ether followed by aqueous work-up and vacuum distillation produced the methylamine derivative $H_2C_5Me_4$=$CHCH_2NHMe$ (**7c**) in a yield of 91%. The overall isolated yield of **7c** based on **4** was 62%.

^1H and ^{13}C NMR spectroscopy revealed that, in contrast to the compounds with R = ^{i}Pr and ^{t}Bu, the dominant isomer is the isomer with the exocyclic double bond (G, figure 2.2), $H_2C_4Me_4C$=CHR' (R' = CN, **8**; CH_2NH_2, **9**; CH_2NHCHO, **10**; CH_2NHMe, **7c**). This is probably a result of the stability of the conjugated system in **8**. In the subsequent derivatisations, employing basic or neutral conditions, this exocyclic double bond is retained. Acid-base treatment of **7c** followed by Kugelrohr distillation yielded exclusively the corresponding mixture of endocyclic double bond isomers (D – F, figure 2.2), showing that these systems do isomerise under acidic conditions.

2.1.2 Catalyst precursor synthesis

Cyclopentadienyl-amide titanium dichlorides can be prepared from the cyclopentadiene-amine ligand with $TiCl_4$ in the presence of a base (NEt_3).[13] For tetramethylcyclopentadiene-amine ligands the synthesis in general starts from the dilithio- or di(magnesiochloride) salts of the ligand with $TiCl_4$, but this leads to low yields of the desired dichlorides.[8f,22] Using the dilithio or di(magnesiochloride) salt of the ligand with $TiCl_3(THF)_3$ followed by a subsequent oxidation step with AgCl to oxidise the Ti(III) centre to Ti(IV) leads to higher yields (scheme 2.4).[8c] Oxidation reagents like CH_2Cl_2[8n,23] or $PbCl_2$[8n,24] work equally well.

Using the dilithio salt (prepared via dilithiation of the cyclopentadiene-amine ligand **7a** with ^{n}BuLi in pentane), and $PbCl_2$ as oxidizing agent (scheme 2.4),[8n,24] results in the corresponding *tert*-butylamide derivative $[C_5Me_4(CH_2)_2N^tBu]TiCl_2$ (**3a**) in 33% isolated yield. The corresponding isopropylamide derivative $[C_5Me_4(CH_2)_2N^iPr]TiCl_2$ (**3b**) was obtained in 60% isolated yield using the same procedure. The yield of the methylamide derivative $[C_5Me_4(CH_2)_2NMe]TiCl_2$ (**3c**) was highly dependent on the isomer composition of the ligand used. Compound **3c** was obtained in 39% yield when using the ligand **7c** that was previously isomerised to the mixture of isomers with exclusively



7a, R = ^{t}Bu
7b, R = ^{i}Pr
7c, R = Me

3a, R = ^{t}Bu
3b, R = ^{i}Pr
3c, R = Me

Scheme 2.4

endocyclic double bonds (*vide supra*). The use of portions of **7c** that consists predominantly of the isomers with an exocyclic double bond resulted in significantly lower yields of **3c** (10-20%).

The titanium complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The spectroscopic features of the compounds are in accordance with monomeric, C_s symmetric complexes. In comparing the three species, the most prominent feature is that the ^{13}C NMR resonance of the bridge NCH_2 for R = Me (**3c**, δ 79.5 ppm) is considerably downfield from the corresponding resonances in the compounds with R = ^{i}Pr, ^{t}Bu (δ 67.7 and 69.4 ppm, respectively). The complex **3c** (impure and with unspecified yield) was suggested by Mena *et al.* to be one of the products in the thermolysis of $(C_5Me_5)Ti(NMe_2)Cl_2$.[15] The observed NMR spectra for **3c** as synthesised here corroborate this identification.

2.1.3 Olefin homopolymerisation with $[C_5Me_4(CH_2)_2NR]TiCl_2$/MAO

Compounds **3** and **1a** were screened for the homopolymerisation of ethene (toluene solvent, MAO cocatalyst, Al/Ti = 500, [Ti] = 6.0×10^{-5}, 2 bar ethene, 50°C, 30 min. run time; table 2.1). The high activity of these systems resulted in a relatively large spread in the observed activities of the runs, with a general activity trend of **3a** > **3b** > **1a** > **3c**. The molecular weights for the polymers decrease in the order **3c** > **3b** > **1a** > **3a**. Both trends agree with those observed for $[C_5Me_4(SiMe_2)NR]TiCl_2$/MAO catalysts.[1e]

Surprisingly, the $[C_5Me_4(CH_2)_2NR]TiCl_2$/MAO catalysts with R = ^{t}Bu (**3a**) and R = ^{i}Pr (**3b**) were inactive in the homopolymerisation of propene. Only for R = Me (**3c**) production of atactic polypropene was observed. This is remarkable, as the catalyst with

Table 2.1. Ethene homopolymerisation experiments with $[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = ^{t}Bu, **3a**, ^{i}Pr, **3b**, Me, **3c**) and $C_5Me_4(SiMe_2)N^{t}Bu]TiCl_2$ (**1a**)/MAO.[a]

Run No.	*Catalyst*	*Yield*	*Activity*[b]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
1	**3a**	20.4	2040	115	46	2.5
2	**3a**	11.8	1180	203	54	3.8
3	**3b**	15.8	1580	369	86	4.3
4	**3b**	14.1	1410	347	81	4.3
5	**3c**	6.4	638	787	143	5.5
6	**3c**	4.8	480	573	100	5.7
7	**1a**	11.0	1100	253	91	2.8
8	**1a**	10.9	1090	303	101	3.0

[a] Toluene solvent, Al/Ti = 500, [Ti] = 4.0×10^{-5} M, 2 bar ethene, 50°C, 30 min. run time; [b] kg (PE) × mol Ti^{-1} × bar^{-1} × h^{-1}.

Table 2.2. Propene homopolymerisation experiments with $[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = ^{t}Bu, **3a**, ^{i}Pr, **3b**, Me, **3c**) and $[C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**1a**)/MAO.[a]

Run. No.	*Catalyst*	*Yield*	*Prod.*[a]	M_w $(\times 10^3)$	M_n $(\times 10^3)$	M_w/M_n
9	**3a**	–	inactive	–	–	–
10	**3b**	–	inactive	–	–	–
11	**3c**	18.9	2520	102	55	1.9
13	**3c**	17.1	2280	110	56	2.0
13	**1a**	59.0	10000	140	78	1.8

[a] Toluene solvent (250 mL), Al/Ti = 500, [Ti] = 6.0×10^{-5} M, 2 bar propene, 50°C, 30 min. run time; [b] kg (PP) × mol $Ti^{-1} \times h^{-1}$.

the $SiMe_2$-bridge $[C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**1a**)/MAO, readily catalyses the homopolymerisation of propene under the same conditions.

It puts into perspective the observation by Stevens *et al.* that for R = ^{t}Bu (**3b**) the catalyst is highly active in ethene/1-octene copolymerisation, but that the amount of incorporated comonomer appears to be very small.[8d] The fact that the analogous system with the unsubstituted Cp-ligand, $[C_5H_4(CH_2)_2N^tBu]TiCl_2$ (**2c**)/MAO, also readily homopolymerises propene[13] suggests that steric factors may be important here. These factors will be discussed in section 2.1.6.

As reported previously,[24b] the polypropene formed by **1a**/MAO is syndiotactically enriched. In the sample prepared in our experiments the *mm* : *rr* ratio is 14 : 37 and

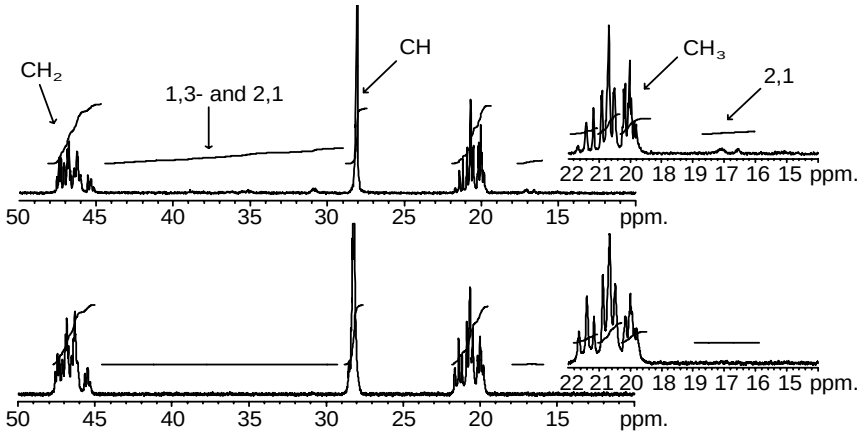


Figure 2.3. ^{13}C NMR spectra of the polypropenes produced by **1a**/MAO (run 13, upper spectrum, right: enlargement of the methyl region) and **3c**/MAO (run 11, lower spectrum).

contains about 2% regioerrors (2,1-insertions), as seen by ^{13}C NMR spectroscopy (figure 2.3, see also 1.2.2).[24b] In contrast, the polypropene produced by the **3c**/MAO catalyst is nearly atactic (ratio of *mm* : *rr* triads is 22 : 28) and noticeably more regioregular (< 0.5% regioerrors). In both polymers no resonances could be observed for 1,3-insertions.

Systems based on the cyclopentadienyl-amido ligand in general show a bias towards syndiotactic enrichment, and 2 – 3% regioerrors are usually found in these polypropylenes.[24b] Less sterically encumbered ligands, compared to **1a**/MAO, give a modest increase in regioselectivity, while stereoselectivity is hardly affected.[24b] In this light it is strange that the polymer obtained with **3c**/MAO is much more regioregular, but does not show a significant bias towards syndiotacticity. The observations suggest that the stereoregularity in these catalyst systems is connected to its regioregularity.[25]

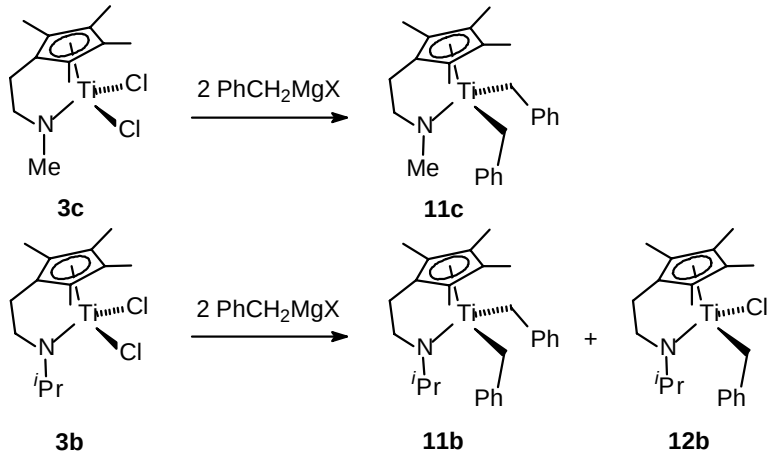
2.1.4 Synthesis of dialkyl derivatives

It is remarkable that **3a** and **3b** with MAO-cocatalyst are unable to polymerise propene, whereas under the same conditions the analogues **1a** and **3c** both are active. In section 1.3 was shown that, besides ligand effects, the counterion/activator can also considerably affect the polymerisation characteristics of the catalyst. To study these effects, the cyclopentadienyl-amide titanium dichlorides **3b** and **3c** were converted to dialkyls, which were activated with borane and borate reagents and tested in olefin homopolymerisation.

Reaction of **3c** with two equivalents of $PhCH_2MgBr$ in diethyl ether, followed by evaporation of the solvents and extraction with pentane, yielded $[C_5Me_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**11c**) in 90% yield. The spectroscopic features of this compound are in accordance with C_s symmetry. As for the dichloride **3c** the N-CH_2 carbon for **11c** is found at a relatively low field (δ 71.9 ppm). The two, diastereotopic, protons of the Ti-CH_2-groups of the benzyl substituents are observed as a single signal at δ 2.16 ppm in the ^1H NMR spectrum, the corresponding carbon resonance is found at δ 73.5 ppm.

Performing the same reaction with **3b** invariably resulted in the formation of a mixture containing two major components. The minor constituent of these was identified (by ^1H NMR spectroscopy) as $[C_5Me_4(CH_2)_2N^iPr]Ti(CH_2Ph)_2$ (**11b**), whereas the major compound probably is the monobenzyl complex $[C_5Me_4(CH_2)_2N^iPr]Ti(Cl)(CH_2Ph)$ (**12b**). A longer reaction time did not result in a better yield. Unfortunately neither **11b** nor **12b** could be purified by crystallisation.

In the ^1H NMR spectrum of **12b** the resonances of the Cp*-methyls are observed as four singlets, and for the bridge a complex pattern is observed. The Ti-CH_2 resonance is observed as two doublets at δ 2.21 and 2.08 ppm ($^2J_{HH}$ = 10.7 Hz). For the C_s symmetrical dibenzyl **11b** two signals for the Cp*-methyls are observed, as well as, two

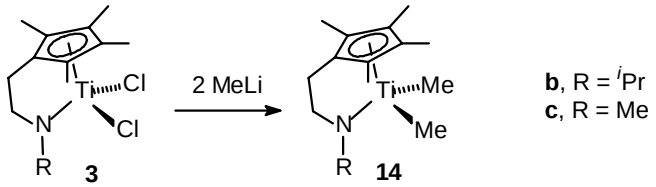


Scheme 2.5.

triplets for the bridging $(CH_2)_2$-unit. The Ti-CH_2 resonance of **11b** is observed as two doublets at δ 2.08 and 1.99 ppm ($^2J_{HH}$ = 10.3 Hz).

The problems encountered in the synthesis of **11b** may have steric reasons. To see if dialkyl species are accessible, **3b** was reacted subsequently with one equivalent $PhCH_2MgBr$ and one equivalent MeLi in diethyl ether. After evaporation of the solvents, extraction with pentane and evaporation of the solvents an orange oil was obtained. The oil was identified (by ^1H and ^{13}C NMR spectroscopy) as a mixture of $[C_5Me_4(CH_2)_2N^iPr]Ti(Me)(CH_2Ph)$ **13b** and $[C_5Me_4(CH_2)_2N^iPr]TiMe_2$, **14b** (*vide infra*, in a 95:5 ratio) and some unidentified compounds. For **13b** the signals for the four Cp*-methyls are observed as four separate peaks in the ^1H NMR spectrum. Two singlets are observed for the two protons of the Ti-CH_2 group at δ 1.14 and 1.12 ppm. The Ti-Me is observed as a singlet at δ 0.31 ppm.

The dimethyls $[C_5Me_4(CH_2)_2N^iPr]TiMe_2$ (**14a**) and $[C_5Me_4(CH_2)_2NMe]TiMe_2$ (**14c**) were accessible by reaction of respectively **3b** and **3c** with 2 equivalents of MeLi in diethyl ether. Evaporation of the solvents and subsequent extraction with pentane and crystallisation from this solvent yielded the dimethyl species in respectively 30 and 35% isolated yield. Intermediates during the synthesis appear to be light-sensitive; when the reaction is performed under ambient light, black decomposition products are formed, resulting in lower isolated yields.[26] The high solubility of the products also contributes to the low isolated yields of these reactions. Both compounds were characterised by ^1H and ^{13}C NMR spectroscopy. Again the signal for the N-CH_2 carbon in **14c** is located at a relatively low field (as observed for the dichloride analogues, *vide infra*). The signal is found at δ 73.4 ppm in **14c**, whereas the corresponding carbon in **14b** is found at δ 60.9 ppm.



Scheme 2.6.

Reaction of **14b** and **14c** with $B(C_6F_5)_3$ in C_6D_5Br yields the contact ion pairs $[\{C_5Me_4(CH_2)_2N^iPr\}TiMe][MeB(C_6F_5)_3]$ and $[\{C_5Me_4(CH_2)_2NMe\}TiMe][MeB(C_6F_5)_3]$ (in ^{19}F NMR spectra $\Delta\delta(F_p–F_m)$ = 4.33 and 4.76 ppm, respectively).[27] Addition of a few drops of 1-hexene to these solutions resulted in fast and complete conversion to poly(1-hexene).

These observations are of interest since a) the coordination of the anion to the metal centre apparently does not hinder an incoming monomer and b) in contrast to the **3b**/MAO couple, **14b**/$B(C_6F_5)_3$ is able to homopolymerise 1-alkenes. This suggests that not only the steric requirements of the ligand, but also the mode of activation is of importance for these systems.

2.1.5 Olefin homopolymerisation with $[C_5Me_4(CH_2)_2NR]TiR_2$ activated with borane and borate reagents

Ethene homopolymerisation experiments with the dimethyl compounds, activated with a small excess of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) or the anilinium borate $[PhNMe_2H][B(C_6F_5)_4]$ were performed (table 2.3). All catalysts were active in ethene

Table 2.3. Ethene homopolymerisation experiments with $[C_5Me_4(CH_2)_2N^iPr]TiMe_2$ (**14b**) and $[C_5Me_4(CH_2)_2NMe]TiMe_2$ (**14c**) with $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$ activator[a]

Run. No.	*Catalyst*	*Activator*	*Yield*	*Prod.*[a]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
14	**14c**	$B(C_6F_5)_3$	0.66	528	760	190	4.0
15	**14c**	$B(C_6F_5)_3$	0.21	168	190	80	2.4
16	**14c**	$[PhNMe_2H][B(C_6F_5)_4]$	3.10	2464	1010	450	2.2
17	**14c**	$[PhNMe_2H][B(C_6F_5)_4]$	5.70	4584	1120	550	2.0
18	**14b**	$B(C_6F_5)_3$	0.88	704	890	320	2.8
19	**14b**	$B(C_6F_5)_3$	0.92	736	760	190	4.0
20	**14b**	$[PhNMe_2H][B(C_6F_5)_4]$	4.30	3408	1050	570	1.8
21	**14b**	$[PhNMe_2H][B(C_6F_5)_4]$	3.60	2856	1110	560	2.0

[a] Toluene solvent (250 mL), [Ti] = 1.0×10^{-5} M, 2 bar ethene, 50°C, 30 min. run time; [b] kg (PE) $\times$ mol^{-1} $\times$ bar^{-1} $\times$ h^{-1}.

Table 2.4. Propene homopolymerisation experiments with $[C_5Me_4(CH_2)_2N^iPr]TiMe_2$ (**14b**) and $[C_5Me_4(CH_2)_2NMe]TiMe_2$ (**14c**) with $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$ activator[a]

Run. No.	*Catalyst*	*Activator*	*Yield (g)*	*Prod.*[a]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
22	**14c**	$B(C_6F_5)_3$	18.6	14,900	360	220	1.6
23	**14c**	$B(C_6F_5)_3$	9.0	7,200	230	150	1.5
24	**14c**	$[PhNMe_2H][B(C_6F_5)_4]$	11.1	8,900	180	40	4.5
25	**14c**	$[PhNMe_2H][B(C_6F_5)_4]$	30.5	24,400	340	100	3.4
26	**14b**	$B(C_6F_5)_3$	4.5	3,600	140	80	1.8
27	**14b**	$B(C_6F_5)_3$	5.1	4,100	120	70	1.7
28	**14b**	$[PhNMe_2H][B(C_6F_5)_4]$	28.4	22,700	360	110	3.3
29	**14b**	$[PhNMe_2H][B(C_6F_5)_4]$	31.0	24,800	350	110	3.2

[a] Toluene solvent (250 mL), activator/Ti = 1.1, [Ti] = 1.0×10^{-5} M, 2 bar propene, 50°C, 30 min. run time; [b] kg (PP) $\times$ mol^{-1} $\times$ h^{-1}.

homopolymerisation, but the high activity and the absence of impurity scavengers results in a rather large spread in activity data and broadening of the polydispersity (see section 1.2.1). In general, the catalysts generated by the reaction of the dimethyl precursors with $[PhNMe_2H][B(C_6F_5)_4]$ have a higher activity than with $B(C_6F_5)_3$. The activities and molecular weights are of the same order of magnitude as the dichloride/MAO systems (table 2.1).

Surprisingly, all catalysts proved active in propene polymerisation, as opposed to the dichloride/MAO systems. Again there is a large spread in the activity data, probably due to the absence of scavenger (see section 1.2.1). Table 2.4 shows the results from the propene polymerisation experiments.

Table 2.5. Stereo- and regioselectivity data for the polymers produced by $[C_5Me_4(CH_2)_2N^iPr]TiMe_2$ (**14b**) and $[C_5Me_4(CH_2)_2NMe]TiMe_2$ (**14c**) with $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$ activator

Run	*Cat*	*Act*	*mm*	*mr-rm*	*rr*	*%regio errors*
11[a]	**3c**	MAO	22	50	28	<0.5
22	**14c**	$B(C_6F_5)_3$	18	46	36	4
25	**14c**	$[PhNMe_2H][B(C_6F_5)_4]$	21	48	31	4
27	**14b**	$B(C_6F_5)_3$	16	50	34	2
28	**14b**	$[PhNMe_2H][B(C_6F_5)_4]$	16	50	34	3

[a] Data from table 2.2.

The $[PhNMe_2H][B(C_6F_5)_4]$ activated systems have a higher activity than the $B(C_6F_5)_3$ activated systems, and they produce polymers with a broader molecular weight distribution. ^{13}C NMR spectroscopy of the produced polymers shows that, in contrast to the polymer produced by **3c**/MAO (which is atactic, with less than 0.5% regioerrors) the polymers produced by **14c** (with $B(C_6F_5)_3$ or $[PhNMe_2H][B(C_6F_5)_4]$ activator) are slightly syndiotactically enriched (*mm* : *rr* respectively 18 : 36 and 21 : 31) and contain about 4% regioerrors (table 2.7). Also the polymers produced by **14b** are slighly syndiotactically enriched with 2-3% regioerrors. In all polymers no 1,3 insertions or end groups were observable in the ^{13}C NMR spectra.

2.1.6 Discussion

A new route to ethylene-bridged tetramethylcyclopentadienyl-amide ligands was devised that gave access to a series of $[C_5Me_4(CH_2)_2NR]TiX_2$ (R = Me, ^{i}Pr, ^{t}Bu; X = Cl, Me) precatalysts. In comparative propene homopolymerisation experiments, the catalyst performance was found to depend strongly on the amide/activator combination. The MAO-activated systems appear to act as catalysts with a sterically constricted active site: propene is only homopolymerised by the catalyst with the smallest amide substituent (R = Me), and there the unusually high regioselectivity of the resulting polymer (compared with that usually observed for Cp-amido Ti catalysts[24b]) suggests a site with very limited spatial freedom. In contrast, the borate activated systems are all active, irrespective of the amide substituent, and all produce polymer with similar concentrations of regioerrors. It seems to be an indication of significant differences in cation-anion interaction between the two different activator types. As the actual nature of the MAO-derived anion and its interactions is still unclear, and as the corresponding precatalysts with the $SiMe_2$-bridge do not seem to show these effects, it may be insightful to make a structural comparison between the two catalyst systems.

Comparing the structures of $[C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**1a**) and $[C_5Me_4(CH_2)_2N^tBu]TiCl_2$ (**3a**), it can be seen that the Cp(centroid)-Ti-N 'bite angles' of the two ligand systems are identical, 107.8° for Me_2Si,[28] 107.9° for $(CH_2)_2$, as are the Ti-N distances (1.909 Å for both).[3,28] One difference may be found in the distribution of the angles around the planar amide nitrogen. A smaller Ti-N-C(^{t}Bu) angle is expected for the ethylene bridge, compare e.g. Ti-N-C(^{t}Bu) for $[C_5H_4(CH_2)_2N^tBu]TiCl_2$ (**2a**)[13b] of 124.1° with the 128.3° for $[C_5Me_4(Me_2Si)N^tBu]TiCl_2$ (**1a**).[29] This would bring the substituent on the amide function closer to the active site in the case of the catalyst with the ethylene-bridged ligand, and would increase the steric hindrance in the active site. Reducing the size of the amide substituent from ^{t}Bu to ^{i}Pr should lessen the steric hindrance around the metal centre, but this also leads to a further significant reduction of the Ti-N-C(R) angle, as follows from the structures of $[C_5H_4(CH_2)_2NR]TiCl_2$ (R = ^{t}Bu (**2a**),[13b] 124.1°, R = ^{i}Pr (**2b**),[13] 114.2°). In all cases this suggests that the amido

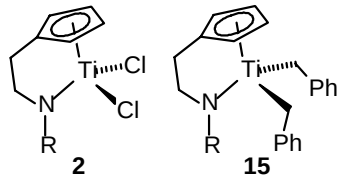
substituent in these complexes is positioned close to the active centre, and that the proximity of an anion of suitable geometry (which will be close to the cationic metal centre due to Coulombic interactions) may further hinder the incoming monomer and thereby prevent or restrict the polymerisation process. Although there is as yet no definite proof (mainly because the nature and interactions of the MAO-derived anion are not known), this geometric difference between the $SiMe_2$- and $(CH_2)_2$-bridged catalysts systems may lie at the root of the observed catalyst behaviour.

2.2 Effect of the counterion on polymerisation with $[C_5H_4(CH_2)_2NR]TiR$-cation

A large effect of activator on the propene homopolymerisation behaviour was observed by Sinnema *et al*. with the $[C_5H_4(CH_2)_2NR]TiX_2$ (**2**)/activator systems (X = Cl, CH_2Ph).[13] When switching from dichloride/MAO (2/MAO) to dibenzyl (**15**)/$B(C_6F_5)_3$ activation, an 8-fold increase of the molecular weight of the polymer was observed with the catalyst with an ^{i}Pr substituent on the nitrogen, while for the Me and ^{t}Bu substituted catalysts only a 1.4 – 2 fold increase was found. The change also affected the stereoregularity of the polypropylene formed. The effect is again most pronounced with the catalyst with R = ^{i}Pr. With **2b**/MAO nearly atactic polypropene (*mm* : *rr* = 21.4 : 24.2) is produced, whereas the polypropene produced with **15b**/$B(C_6F_5)_3$ was significantly syndiotactically enriched (*mm* : *rr* = 14.8 : 35.9). With the Me and ^{t}Bu substituted catalysts the stereoselectivity was hardly affected.

The combination of these effects (which reflect the processes taking place at the metal during catalysis) suggests a large influence of the counterion. They were ascribed to the cation-anion interaction that is disfavouring chain transfer relative to chain growth, but also affects the stereoregularity of the resulting polymers.

In view of these observations we sought to design a series of experiments that could help to elucidate the effect of the anion on the polymerisation characteristics of the cation. These experiments are presented in the following paragraphs.



2 **15**

Figure 2.4. Cyclopentadienyl-amide systems.

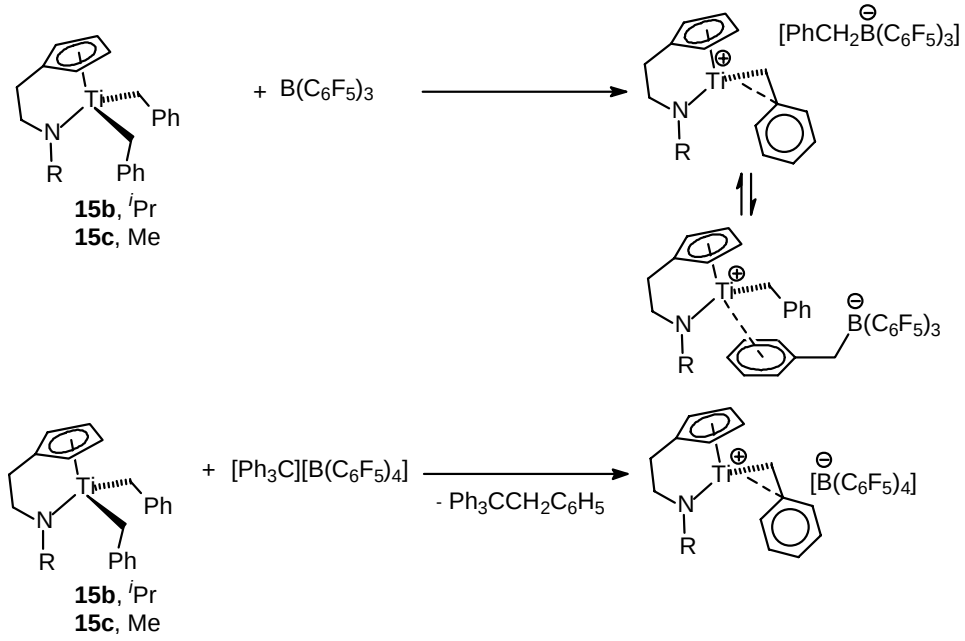
2.2.1 Polymerisation activity

The effect on propene polymerisation is most pronounced between the catalysts with the R = Me (**15c**) and the R = ^{i}Pr (**15b**) substituents. There is an inverse in trend in the productivities when changing from MAO (which is believed to provide a weakly

coordinating anion) to the benzyl-tris(pentafluorophenyl) borate anion (which can coordinate to cationic metal centres via the arene group of the benzyl moiety, scheme 2.7).[27] This, in combination with the observed effects of the anion on the molecular weight and tacticity of the polymers, prompted us to compare **15b** and **15c** with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$),[30,31] and triphenylcarbyl ('trityl') tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$)[31a,32] activators. The former results in a catalyst with the (coordinating) $[PhCH_2B(C_6F_5)_3]$-counterion, the latter with in one with the weakly coordinating $[B(C_6F_5)_4]$-counterion.[33]

The results for the propene homopolymerisations are shown in table 2.6. The polymerisations were run without the use of scavenger, since the commonly used aluminiumalkyls may interfere with the polymerisation characteristics of the catalyst (see also section 1.2.1).[35] As a consequence, the experiments were run at a relatively high catalyst concentration, and multiple runs were performed for each system to check reproducibility (see table 2.6).

The runs using $B(C_6F_5)_3$ as activator were all isothermal. With these systems, the polymerisation appeared to start slowly. With the tetrakis(pentafluorophenyl)borate anion the polymerisations start violently exothermic. For **15b**/$[Ph_3C][B(C_6F_5)_4]$ the temperature of the reaction mixture increased by 40-50° within 30 seconds. During the run the consumption of propene is faster than replenishment: the pressure drops from 2.0×10^5 Pa to 0.5×10^5 Pa. For **15c**/$[Ph_3C][B(C_6F_5)_4]$ the polymerisation is less



Scheme 2.7.

Table 2.6. Polymerisation activity of $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$ (R = ^{i}Pr, **15b**; R = Me, **15c**) with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ activator.[a]

No.	*Cat.*	*Activator*	*Yield (g)*	*Prod.*[b]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
30	**15b**	$B(C_6F_5)_3$	18.7	2500	113	61	1.8
31	**15b**	$B(C_6F_5)_3$	24.7	3300	88	48	1.8
32	**15b**	$B(C_6F_5)_3$	20.0	2650	109	59	1.8
33	**15b**	$B(C_6F_5)_3$	21.5	2850	99	53	1.9
			Av.[c]	2850	102	55	1.8
34	**15b**	$[Ph_3C][B(C_6F_5)_4]$	51.3	6800	80	32	2.5
35	**15b**	$[Ph_3C][B(C_6F_5)_4]$	53.6	7000	92	37	2.5
36	**15b**	$[Ph_3C][B(C_6F_5)_4]$	52.1	6900	98	44	2.2
37	**15b**	$[Ph_3C][B(C_6F_5)_4]$	52.9	7050	84	37	2.3
38	**15b**	$[Ph_3C][B(C_6F_5)_4]$	52.7	6950	93	39	2.4
			Av.[c]	6950	92	39	2.4
39	**15c**	$B(C_6F_5)_3$	7.6	1000	753	173	4.4[d]
40	**15c**	$B(C_6F_5)_3$	6.7	900	676	143	4.7[d]
41	**15c**	$B(C_6F_5)_3$	7.2	950	619	125	5.0[d]
42	**15c**	$B(C_6F_5)_3$	6.4	850	730	172	4.3[d]
			Av.[c]	900	695	153	4.5
43	**15c**	$[Ph_3C][B(C_6F_5)_4]$	34.3	4550	156	50	3.1
44	**15c**	$[Ph_3C][B(C_6F_5)_4]$	35.7	4750	148	46	3.3
45	**15c**	$[Ph_3C][B(C_6F_5)_4]$	31.0	4100	196	74	2.7
46	**15c**	$[Ph_3C][B(C_6F_5)_4]$	35.0	4600	191	74	2.6
47	**15c**	$[Ph_3C][B(C_6F_5)_4]$	35.3	4550	166	56	3.0
48	**15c**	$[Ph_3C][B(C_6F_5)_4]$	35.4	4550	177	70	2.5
			Av.[c]	4500	172	62	2.8

[a] Toluene solvent (200 mL), activator/Ti = 1.5, [Ti] = 75×10^{-6} M, 2 bar propene, 50°C, 30 min. run time; [b] kg (PP) × mol Ti^{-1} × h^{-1}; [c] Average value of multiple measurements; [d] Bimodal distribution.

exothermic and the pressure is maintained better. For **15b** the change from borane to borate activator leads to an increase in productivity of a factor of 2.3; for **15c** the productivity is increased by a factor 4.9.

The difference in activity between **15b** and **15c** with the same activator shows that **15b** is consistently more active than **15c**. For the $B(C_6F_5)_3$ activated systems, the difference between **15b** and **15c** is approximately a factor 3. For the borate anion, the

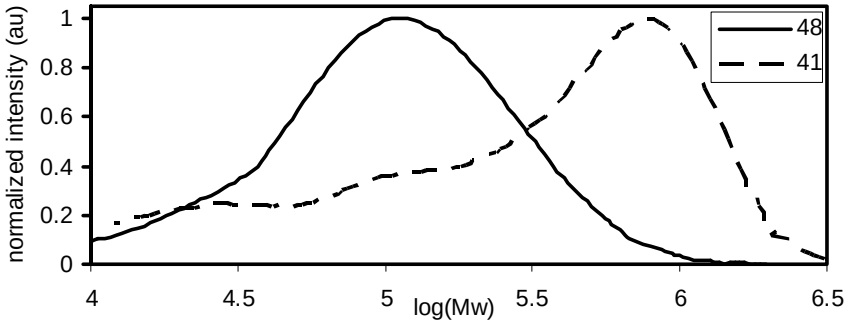


Figure 2.5. GPC traces (normalised) of samples produced by $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**15c**) with $B(C_6F_5)_3$ (run 41) and $[Ph_3C][B(C_6F_5)_4]$ (run 48) activator.

difference is a factor 1.5. This is in contrast with the experiments in which **2b** and **2c** were activated by MAO, where **2c** showed a higher activity (by a factor 2).[13]

The effect of the activator on the molecular weight is most pronounced with precursor **15c**. The M_w of the polymer obtained from **15c**/$B(C_6F_5)_3$ is 4.3 times higher than with **15c**/$[Ph_3C][B(C_6F_5)_4]$. This clearly shows that the anion has a large effect on the polymerisation behaviour of the cation in this case. When compared to the weakly coordinating $[B(C_6F_5)_4]^-$, the coordinative ability of the $[PhCH_2B(C_6F_5)_3]^-$ apparently results in an active site in which chain transfer is disfavoured with respect to monomer insertion. For **15c**/$[Ph_3C][B(C_6F_5)_4]$ the polydispersities indicate single site behaviour, but the polydispersities of the borane activated runs are clearly higher than 2. Inspection of the GPC traces (see figure 2.5) shows that the polymer consists of 2 fractions, one with a M_w of approximately 7.5×10^5 and one with a much lower M_w (approximately 1×10^5). This suggests that there may be at least two distinct active species in this system.

For the R = ^{i}Pr systems (**15b**) the counterion seems to have a smaller effect on the molecular weight of the polymer produced. All the polymers produced are of moderate molecular weight ($M_w = 92 - 135 \times 10^3$). The polydispersity of the runs indicates single site behaviour ($M_w/M_n \sim 2$). The values for the borate activated runs are slightly higher than 2, probably due to the high activity (*vide supra* and section 1.2.1).

Analysis of the polypropenes by ^{13}C NMR spectroscopy shows that these are atactic materials. Triad distributions and regioerrors for representative samples are presented in table 2.7. All samples show some syndiotactic enrichment, which is most pronounced in the **15c**/$B(C_6F_5)_3$ system. Changing the anion from $[PhCH_2B(C_6F_5)_3]^-$ to $[B(C_6F_5)_4]^-$ decreases the syndiotactic enrichment somewhat (*rr : mm* ratio going from 41 : 13 to 35 : 18). Apparently the environment of the active site is different with the $[PhCH_2B(C_6F_5)_3]$-anion than with the $[B(C_6F_5)_4]$-anion (as was also concluded based on

Table 2.7. Stereo- and regioselectivity of polymers produced by $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$ (R = ^{i}Pr, **15b**; R = Me, **15c**) with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ activator.

Run No.	*Cat*	*Act*	*mm*	*mr-rm*	*rr*	*%regio errors*
33	**15b**	$B(C_6F_5)_3$	18	47	35	4
38	**15b**	$[Ph_3C][B(C_6F_5)_4]$	15	46	39	7
41	**15c**	$B(C_6F_5)_3$	13	46	41	6
48	**15c**	$[Ph_3C][B(C_6F_5)_4]$	18	47	35	6

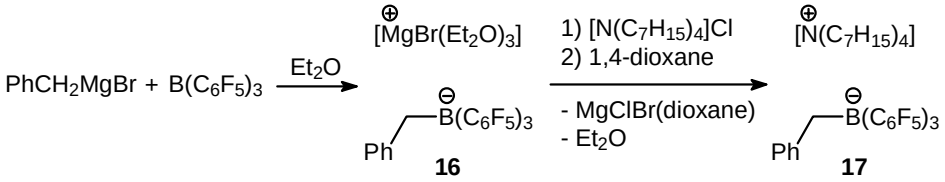
the molecular weight distributions). In all the polymers 4 – 7% regioirregularities are observed, indicating that with all catalyst systems 2,1-propene insertion can occur. Due to the high molecular weight, no endgroups could be observed.

In the experiments described, a large effect of the counterion on the polymerisation behaviour of the cationic catalyst was observed. Especially for the catalyst system with the least substituted ancillary ligand (**15c**) a large effect was observed when switching from a moderately coordinating anion to a weakly coordinating anion.

2.2.2 Counterion synthesis

The above experiments suggest that adjusting the nature of the anion does not only affect catalyst activity, but also the molecular weight and stereoregularity of the polymer. To probe this issue further, we sought a way to exchange the $[B(C_6F_5)_4]$-anion (resulting from activation with $[Ph_3C][B(C_6F_5)_4]$), with the $[PhCH_2B(C_6F_5)_3]$-anion. If the higher coordinating ability of the former anion is indeed the cause of the observed effects, the ratio cation : $[PhCH_2B(C_6F_5)_3]^-$ should have an effect on the properties of the produced polymer.

The benzyl-tris(perfluoro)borate anion ($[PhCH_2B(C_6F_5)_3]^-$) is usually generated *in situ* when a metal dibenzyl pre-catalyst is activated with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$. An independent synthesis of the $[PhCH_2B(C_6F_5)_3]$-anion has not been described, but similar compounds, containing three perfluorinated phenyls and one other aliphatic or aromatic substitutent have been reported.[36] In these procedures, $B(C_6F_5)_3$ is reacted with an appropriate Grignard or lithium alkyl reagent, resulting in the magnesium halide or lithium salt of the borate. The synthesis of $[PhCH_2B(C_6F_5)_3]^-$ should be feasible using the same methodology, starting from benzyl Grignard and $B(C_6F_5)_3$. The cation of the resulting salt should then be exchanged for a suitable cation that (a) makes the resulting ion pair sufficiently soluble in toluene or alkane solvents and (b) is expected to be innocent towards the catalytic system. We therefore aimed at



Scheme 2.8

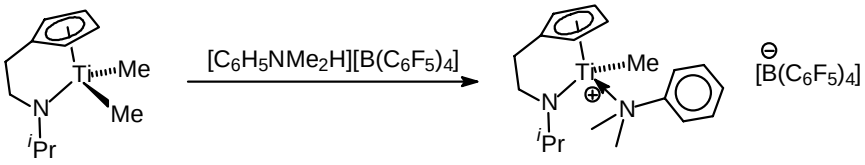
ion pairs of the type $[R_4N][PhCH_2B(C_6F_5)_3]$ with large alkyl groups in the ammonium cation (e.g. heptyl groups).

Benzyl magnesium chloride was reacted with $B(C_6F_5)_3$ in diethyl ether (scheme 2.8), after which the solution was concentrated. Cooling of the solution resulted in the formation of colourless crystals of $[MgBr(Et_2O)_3][PhCH_2B(C_6F_5)_3]$ (**16**) in 52% yield. The chemical shift difference between the *meta* and *para* fluorines in the ^{19}F NMR spectra (CD_2Cl_2, $\Delta\delta(F_p–F_m)$ = 2.8 ppm) is typical for the noncoordinated benzyl tris(perfluorophenyl)borate anion in this solvent.[27] The characteristic B-CH_2 resonance is located at δ 3.01 ppm ($\Delta\nu_{½}$ = 12.3 Hz) in the ^1H NMR spectrum, the corresponding ^{13}C-resonance is located at δ 31.92 ppm ($\Delta\nu_{½}$ = 120 Hz) in the ^{13}C NMR spectrum.

The magnesiumbromide-etherate cation was exchanged for $N(C_7H_{15})_4^+$ by mixing dichloromethane solutions of the magnesium salt **16** and $[N(C_7H_{15})_4]Cl$. The resulting ion pair ($[N(C_7H_{15})_4][PhCH_2B(C_6F_5)_3]$ **17** is soluble in this solvent, the magnesium salt was precipitated using dioxane and was subsequently removed by filtration.[37] After evaporation of the solvent **17** is isolated as a colourless oil in 47% yield. Compound **17** is soluble in common solvents, including benzene, toluene and polar solvents (THF, bromobenzene, diethyl ether, dichloromethane).

The solubility of the ion pair in toluene offers the possibility to observe the uncoordinated anion in an apolar solvent. The signals in the ^{19}F NMR spectrum appear at δ –131.5 (*o*-C_6F_5), –164.5 (*p*-C_6F_5), and –167.5 (*m*-C_6F_5). The shift difference between the *meta* and *para* fluorines in the ^{19}F NMR spectrum is δ 2.93 ppm, as expected for a non-coordinated anion.[27] The B-CH_2 is found at δ 3.29 ppm ($\Delta\nu_{½}$ = 21.2 Hz) in the ^1H NMR spectrum, the corresponding carbon at δ 32.7 ppm ($\Delta\nu_{½}$ = 108 Hz) in the ^{13}C NMR spectrum.

Studies of the coordination behaviour of the benzylborate anion, generated *in situ* via benzyl abstraction by $B(C_6F_5)_3$, to the catalytic species $[\{C_5H_4(CH_2)_2NR\}TiCH_2Ph]^+$ were reported by Sinnema,[13a] but were complicated by fluxional dihapto bonding of the remaining Ti-bound benzyl group. To avoid this problem, it was attempted to study the exchange the anion from $[\{C_5H_4(CH_2)_2NR\}TiMe][B(C_6F_5)_4]$. It may be noted that the generation is performed in bromobenzene-d_5, since the ion pairs are insufficiently soluble in toluene-d_8 to allow for NMR spectroscopic studies.



Scheme 2.9.

Reaction of $[C_5H_4(CH_2)_2NR]TiMe_2$ (**18**) with $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene invariably resulted in solutions with prevailingly paramagnetic species, probably resulting from reduction of the metal centre. Generation of the cations (in absence of **17**) with $[PhNMe_2H][B(C_6F_5)_4]$ results in the formation of complex mixtures. For the reaction of $[C_5H_4(CH_2)_2N^iPr]TiMe_2$ (**18b**) with $[PhNMe_2H][B(C_6F_5)_4]$ the ^1H NMR spectrum shows two distinct methyl resonances for the N,N-dimethylaniline coproduct, suggesting coordination of the N,N-dimethylaniline to the cationic titanium centre (scheme 2.9). The reaction of $[C_5H_4(CH_2)NMe]TiMe_2$ (**18c**) with $[PhNMe_2H][B(C_6F_5)_4]$ resulted in the formation of an intractable mixture; coordination of the N,N-dimethylaniline is not observable. These cationic alkyl species are possibly too reactive to survive when generated in the absence of olefinic substrate or Lewis base.

Generation of the cations in the manner as described above, but in the presence of **17** did not lead observable coordination of the benzylborate anion to the cationic metal centres, but results in mixtures of the species described above with **17**. Also in the ^{19}F NMR spectra no evidence for coordination of the benzyl borate anion could be observed.[27]

2.2.3 Polymerisation experiments with extra anion

Despite the unfavourable results in trying to observe the coordination of added benzyl borate to cationic cyclopentadienyl-amide titanium alkyl cations, a series of catalytic polymerisation experiments were performed in which additional borate anion was supplied. The results of the polymerisation experiments in which **17** is added to $[\{C_5H_4(CH_2)_2NMe\}TiCH_2Ph][B(C_6F_5)_4]$ and $[\{C_5H_4(CH_2)_2N^iPr\}TiCH_2Ph][B(C_6F_5)_4]$ are presented in table 2.8.

The spread in activities of these runs is larger than without the addition of the extra anion (table 2.6). This is possibly caused by the fact that now, instead of 2 solutions (activator and procatalyst), 3 solutions have to be injected separately into the autoclave (activator, **17**, and procatalyst, respectively), which may increase the amount of impurities introduced. Also the possible presence of impurities in **17** (which is an oil) may influence the performance.

Table 2.8. Propene polymerisation activity of $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$ (R = ^{i}Pr, **15b**; R = Me, **15c**) with $[Ph_3C][B(C_6F_5)_4]$ activator in presence of **17**.[a]

Run No.	*Cat.*	*Act.*	**17**[b]	*Yield (g)*	*Prod.*[c]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
30 – 33[d]	**15b**	$B(C_6F_5)_3$			2850	102	55	1.8
34 – 38[d]	**15b**	$[Ph_3C][B(C_6F_5)_4]$			6950	90	38	2.4
49	**15b**	$[Ph_3C][B(C_6F_5)_4]$	0.5	47.6	6350	89	41	2.1
50	**15b**	$[Ph_3C][B(C_6F_5)_4]$	0.5	40.9	5900	88	34	2.5
51	**15b**	$[Ph_3C][B(C_6F_5)_4]$	1.0	16.6	2200	61	28	2.2
52	**15b**	$[Ph_3C][B(C_6F_5)_4]$	1.0	13.9	1850	60	27	2.2
39 – 42[d]	**15c**	$B(C_6F_5)_3$			900	695	153	4.5
43 – 48[d]	**15c**	$[Ph_3C][B(C_6F_5)_4]$			4500	172	62	2.8
53	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	13.7[e]	1050	435	225	2.0
54	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	11.6	1500	306	92	3.3
55	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	20.3	2700	186	72	2.6
56	**15c**	$[Ph_3C][B(C_6F_5)_4]$	1.0	0.3	-	n.d.	n.d.	n.d.
57	**15c**	$[Ph_3C][B(C_6F_5)_4]$	1.0	0.1	-	n.d.	n.d.	n.d.

[a] Toluene solvent (200 mL), activator/Ti = 1.5, [Ti] = 75×10^{-6} M, 2 bar propene, 50°C, 30 min. run time; [b] ratio **17** : Ti; [c] kg (PP) × mol $Ti^{-1} \times h^{-1}$; [d] average values from corresponding runs (table 2.6); [e] runtime 52 minutes.

For **15b** with 0.5 equivalents of **17** the runs are still strongly exothermal (a temperature rise of 35°C is observed). With 1.0 equivalent the runs are nearly isothermal (a temperature rise of < 3°C is observed).

The runs with **15b**/$[Ph_3C][B(C_6F_5)_4]$ with 0.5 and 1.0 eq. **17** clearly show the effect of the benzyl borate anion on the character of the catalyst. With 0.5 eq. the productivity is only slightly lower and the molecular weight of the polymer is not significantly lowered when compared to the borate activated runs without added benzyl borate. With 1.0 eq. **17**, both the activity and molecular weight are lower than observed with **15b**/$B(C_6F_5)_3$. Since both experiments require an extra injection when compared to the runs 30 – 38 (table 2.6), the observed lowering of the activity might well be caused by an increase in impurity-level, although it can not be excluded that the ionic strength of the medium also has an effect on the polymerisation.

With **15c** the effect of the added anion is more dramatic. Using 0.5 equivalent **17** results in a catalytic system with productivities between those of **15c**/$[Ph_3C][B(C_6F_5)_4]$ and **15c**/$B(C_6F_5)_3$, but reproducibility of the runs is very poor. The molecular weight (see figure 2.6) follows the same trend as observed for **15c**/$[Ph_3C][B(C_6F_5)_4]$ (high

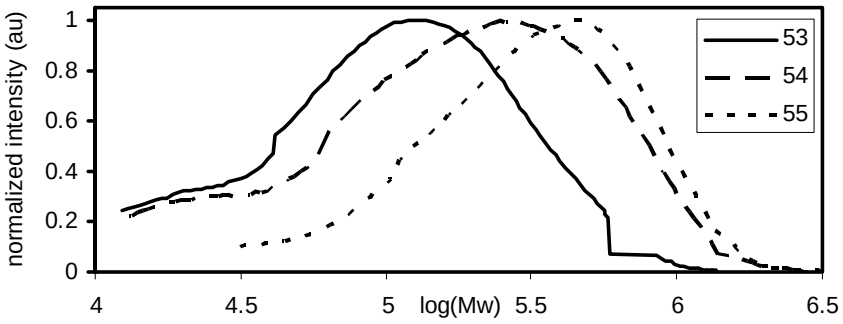


Figure 2.6. GPC traces (normalised) of polymer samples produced by $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**15c**) with $[Ph_3C][B(C_6F_5)_4]$ activator in presence of 0.5 equivalents of **17** (runs 53 – 55).

productivity, low molecular weight) and **15c**/$B(C_6F_5)_3$ (low productivity, high molecular weight). This suggests that small differences in amount of impurities have influenced the actual catalyst concentration, resulting in a relatively large shift in the ratio between cation with and without $[PhCH_2B(C_6F_5)_3]^-$ counterion. With one equivalent the activity of the catalyst is nearly completely quenched. Although again lowering of the activity might be expected due to the extra injection, a complete deactivation due to these impurities seems unlikely.

For the R = ^{i}Pr catalysts (**15b**) the addition of the benzylborate anion shows the expected effect on the tacticity and regioerrors. With 0.5 equivalents the effect is negligible, comparable to the observations on the molecular weight and productivity. With 1.0 equivalent the polymer is comparable to the polymer from **15b**/$B(C_6F_5)_3$.

Table 2.9. Effect of anion addition on tacticity and regioerrors on the polypropenes produced by $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$ (R = ^{i}Pr, **15b**; R = Me, **15c**) with $[Ph_3C][B(C_6F_5)_4]$ activator in the presence of **17**.

No.	*Cat.*	*Act*	**17**[a]	*mm*	*mr/rm*	*rr*	*%regio*
33[b]	**15b**	$B(C_6F_5)_3$	–	18	47	35	4
38[b]	**15b**	$[Ph_3C][B(C_6F_5)_4]$	–	15	46	39	7
50	**15b**	$[Ph_3C][B(C_6F_5)_4]$	0.5	19	45	36	5
51	**15b**	$[Ph_3C][B(C_6F_5)_4]$	1.0	15	46	39	6
41[b]	**15c**	$B(C_6F_5)_3$	–	13	46	41	6
48[b]	**15c**	$[Ph_3C][B(C_6F_5)_4]$	–	18	47	35	6
53	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	19	48	34	3
54	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	16	47	38	3
55	**15c**	$[Ph_3C][B(C_6F_5)_4]$	0.5	16	46	38	5

[a] Ratio **17** : Ti; [b] values from corresponding runs (table 2.7).

The large spread in polymerisation data observed in runs 53 – 55 is also reflected in the tacticity of the produced polymers. The tacticities and regioerrors are in the range observed with **15b**/$B(C_6F_5)_3$ and **15b**/$[Ph_3C][B(C_6F_5)_4]$, but there seems to be no clear trend.

2.2.4 Discussion

The polymerisation experiments described in this section clearly show that in polymerisation not only the ligand set, but also the nature of the anion can greatly influence the polymerisation behaviour of a catalytic system. In the least sterically hindered system $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**20c**) activation with $B(C_6F_5)_3$ leads to a catalyst that gives high molecular weight polypropene, whereas activation with $[Ph_3C][B(C_6F_5)_4]$ leads to polypropene with a lower molecular weight. The tacticity of the resulting polymer is also affected. The runs with $[C_6H_5CH_2B(C_6F_5)_3]^-$ counterion result in a polymer which is significantly more syndiotactically enriched than the runs with the $B(C_6F_5)_4$ anion. For the more sterically hindered system $[C_5H_4(CH_2)_2N^iPr]Ti(CH_2Ph)_2$ (**20b**) the effect of the counterion is less dramatic. This may correlate to the observation by Sinnema that (at least in bromobenzene solvent) both $[\{C_5H_4(CH_2)_2N^iPr\}TiCH_2Ph][PhCH_2B(C_6F_5)_3]$ and $[\{C_5H_4(CH_2)_2N^iPr\}TiCH_2Ph]$-$[B(C_6F_5)_4]$ exist as solvent separated ion pairs.[13] That in the methylamido-system the counterion affects both the molecular weight as well as the microstructure of the polymer suggests a real change in the nature of the catalytically active species. Unfortunately, the experiments with added $[C_6H_5CH_2B(C_6F_5)_3]$-anion were inconclusive, possibly due to the introduction of impurities, which cannot be buffered in experiments without the presence of an impurity scavenger.

2.3 Conclusions

A novel route was devised for the synthesis of ethylene-bridged tetramethylcyclopentadienyl-amide ligand using the commercially available tetramethylcyclopentenone as starting material. The route can be easily adapted to introduce CH_2CH_2X moieties (where X = NHR, NR_2, OR) in other systems as well.

Propene homopolymerisation experiments with both types of ethylene-bridged cyclopentadienyl-amide titanium catalysts (with either tetramethyl- or unsubstituted cyclopentadienyl moiety) showed that in these systems the interplay of ancillary ligand and cocatalyst can strongly affect catalyst performance. That these effects do not only involve catalyst activity, but also the molecular weight and the microstructure of the polymer produced, indicates that both the ligand and the cocatalyst together can shape the nature of the active catalyst species. In order to harness these effects to tune or optimise catalyst performance, a better insight is needed into catalyst-cocatalyst cation-anion interactions.

2.3 Experimental Section

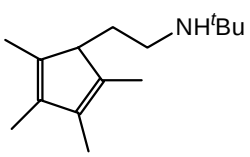
General considerations, syntheses.

The experiments described were performed under an inert nitrogen atmosphere using standard Schlenk and glove-box techniques, except for the aqueous work-up procedures for the organic compounds that were performed under aerobic conditions. Solvents (Aldrich, anhydrous) were passed over a column containing BASF R3-11 supported Cu based scavenger and either a mixture of alumina and 3 Å molsieves (toluene), 4 Å molsieves (pentane, hexane) or alumina (THF, diethyl ether) under nitrogen atmosphere before use. The deuterated solvents THF-d_8, C_6D_6, $C_6D_5CD_3$, (Aldrich) were dried on Na/K alloy and vacuum transferred before use, CD_2Cl_2 and C_6D_5Br were dried on CaH_2 and vacuum transferred before use.

The reagents $LiAlH_4$ (Merck), $PbCl_2$, diisopropylamine, acetonitrile, ethyl formate, ethyl acetate, $[N(C_7H_{15})_4]Cl$ (Acros), ^{n}BuLi (2.5 M in hexane, Aldrich), MeLi (1.4 M in diethyl ether; Aldrich) and MeMgCl (3 M in THF; Aldrich) were used as purchased. The 2,3,4,5-tetramethylcyclopent-2-enone (**4**),[19] $TiCl_3(THF)_3$,[38] the imines $CH_3CH{=}NR$ (R = ^{i}Pr,[39] ^{t}Bu[39,40]), the dichloride $[C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**1a**),[41], the dibenzyls $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**15c**), and $[C_5H_4(CH_2)_2N^iPr]Ti(CH_2Ph)_2$ (**15b**),[13] the dimethyls $[C_5H_4(CH_2)_2NMe]TiMe_2$ (**18c**) and $[C_5H_4(CH_2)_2N^iPr]TiMe_2$ (**18b**),[13b] and $B(C_6F_5)_3$[42] were synthesised according to literature procedures. The N,N-dimethylaniliniumborate $[PhNMe_2H][B(C_6F_5)_3]$, and the trityl borate $[Ph_3C][B(C_6F_5)_3]$ were obtained from Asahi Glass Co. and used as purchased. Grignard reagents were prepared from the corresponding halides with magnesium in diethyl ether or THF.

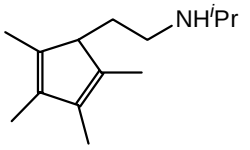
IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrometer. NMR spectra were run on Varian Gemini 200, VXR-300, Mercury Plus 400 and Unity 500 spectrometers. The ^{1}H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ 7.15 ppm for C_6D_6, δ 7.28 ppm for $CDCl_3$; δ 7.30, 7.05, and 6.98 for C_6D_5Br), and the ^{13}C NMR spectra to resonances of the carbon atoms in the deuterated solvents (δ 128 ppm for C_6D_6; δ 125 for $CDCl_3$; δ 130.9, 129.3, 126.2 and 122.2 for C_6D_5Br). Exact mass spectrometry was performed on a JEOL JMS 600 instrument. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of *N-tert*-Butyl-2-(2,3,4,5-tetramethylcyclopentadienyl)ethylamine (7a).



To a solution of diisopropylamine (14 mL, 100 mmol) in 125 mL of THF, cooled to –20°C, was added 40 mL of a 2.5 M solution of ^{n}BuLi in hexane. The stirred mixture was cooled to –80°C and acetaldehyde *N-tert*-butylimine (10.0 g, 100 mmol) was slowly added. After 30 min 2,3,4,5-tetramethylcyclopent-2-enone **4** (13.8 g, 100 mmol) was added and the mixture was stirred for another 30 min at –70°C. Over 1 h the temperature was allowed to rise to –40°C, then $LiAlH_4$ (4.7 g, 125 mmol) was added to the stirred mixture and the temperature was gradually raised to 40°C. After 2 h the mixture was cooled to ambient temperature and water (15 mL) was carefully added. After the grey suspension changed colour to yellow, the mixture was dried with Na_2SO_4 (25 g) and then filtered. The solids were washed with 4 portions of diethyl ether (50 mL each). The filtrates were combined and concentrated. The concentrate (19 g) was dissolved in 50 mL of diethyl ether. To the stirred solution 100 ml 2N HCl was gradually added, keeping the temperature below 25°C. The aqueous phase was first washed with diethyl ether, and then a solution of 10 g of NaOH in water (50 mL) was added followed by extraction with diethyl ether. The combined diethyl ether fractions were dried on Na_2SO_4, concentrated and distilled to give 4.66 g (21.0 mmol, 21%) of **7a** as a mixture of isomers (bp 65 – 70°C, 0.03 mmHg). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 2.70 – 1.85 (CH_2 & C*H*Me), 1.80 – 1.68 (=C*Me*), 1.10 – 0.93 (^{t}Bu Me & CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 300 MHz, 25°C) δ 137.4 – 131.0 (=C–), 52.7, 49.1 and 47.0 (ring CH), 47.7 (N*C*Me$_3$), 40.5, 39.8 and 35.8 (NCH_2), 26.4 (C*Me*$_3$), 25.4 and 25.0 (C*CH*$_2$), 11.7 – 8.5 (8 × Me).

Synthesis of *N-iso*-Propyl-2-(2,3,4,5-tetramethylcyclopentadienyl)ethylamine (7b).

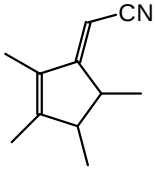


To a solution of diisopropylamine (10.5 mL, 75 mmol) in 100 mL of THF, cooled to –20°C, was added 30 mL of a 2.5 M solution of ^{n}BuLi in hexane (75 mmol). After 15 minutes acetaldehyde *N-iso*-propylimine (6.38 g, 75 mmol) was added, followed by 2,3,4,5-tetramethylcyclopent-2-enone **4** (10.35 g, 75 mmol). Over 1.5 h the mixture was allowed to warm to 10°C. The mixture was washed with water (2 × 10 mL), dried over Na_2SO_4 and concentrated to give 15 g of the crude alcohol **5b**. This was dissolved in 30 mL of diethyl ether and slowly added to a suspension of $LiAlH_4$ (3 g, 80 mmol) in 100 mL of diethyl ether. After stirring for 4 h at ambient temperature, water (8 mL) was slowly added. After standing overnight the white suspension was dried over Na_2SO_4 and filtered. The filtrate was worked up as described above for the preparation of **7a**. Distillation yielded 6.02 g (29.0 mmol, 39%) of **7b** as a mixture of three isomers (bp 63 – 65°C, 0.03 mmHg).

^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ 2.90 – 2.10 (CH_2 & C*H*Me), 1.94 – 1.72 (=C*Me*), 1.18 – 0.95 (^{i}Pr Me & CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 75 MHz, 25°C) δ 137.5 – 130.9 (10 × =*C*–), 52.4, 49.0 and 47.0 (ring CH), 46.0 (NCH), 45.4, 44.6 and 40.5 (NCH_2), 25.7, 24.6 and 24.2 (C*C*H_2), 20.4 (^{i}Pr Me), 11.7 – 8.5 (10 × Me). Exact MS calcd for $C_{14}H_{25}N$: 207.199, observed 207.198.

Attempted dehydration of $HC_5Me_4(OH)CH_2CH{=}NR$ (R = ^{t}Bu, 5a; ^{i}Pr, 5b).
The crude alcohols **5a** and **5b** (characterised in their ^{1}H NMR spectra by a triplet at 7.73 ppm, $^3J_{HH}$ = 4.2 Hz, for the imine proton), obtained as described above in the synthesis of **7b**, were subjected to attempts to effect acid-catalysed dehydration. For R = ^{t}Bu, aqueous HCl / aqueous NaOH acid-base treatment of a diethyl ether solution of the alcohol led to recovery of cyclopentenone **4**. Stirring an diethyl ether solution of the alcohol on P_2O_5 followed by short-path distillation yielded the imine $H_2C_5Me_4CHCH{=}N^tBu$ (**6a**) in about 15% yield based on **4** used initially, still contaminated with about 10% of **5**. For R = ^{i}Pr the acid-base procedure resulted, after evaporation of the diethyl ether solvent, in a product mixture that contained **5** and the imine $H_2C_5Me_4CHCH{=}N^iPr$ (**6b**) in approximately equimolar amounts. **6a**: ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 8.12 (d, $^3J_{HH}$ = 9.5 Hz, 1H, CH=N), 5.92 (d, $^3J_{HH}$ = 9.5 Hz, 1H, C=CH), 2.60 (br q, $^3J_{HH}$ = 7.1 Hz, C*H*Me; the other C*H*Me resonance is obscured), 1.73 and 1.63 (s, 3H each, Me), 1.18 (s, 9H, ^{t}Bu), 1.08 and 0.98 (d, $^3J_{HH}$ = 7.1 Hz, 3H each, CH*Me*).

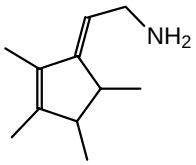
Synthesis of [2,3,4,5-Tetramethyl-cyclopent-2-enylidene]-acetonitrile (8).



To a solution of acetonitrile (6.0 mL, 110 mmol) in THF (125 mL) cooled to –80°C was added 44 mL of a 2.5 M solution of ^{n}BuLi in hexane (110 mmol). After 15 minutes 2,3,4,5-tetramethylcyclopent-2-enone **4** (15 mL, 13.8 g, 100 mmol) was added at –80°C over a period of 45 min. Over 3 h the temperature was allowed to rise to 0°C. Water (25 mL) was added and the organic layer was washed with two portions of water (10 mL). Then 2N HCl (10 mL) was added, the mixture was shaken and after 16 h the layers were separated. The organic phase was washed with brine, dried on Na_2SO_4 and concentrated. The residue was distilled to give 15.8 g (98.0 mmol, 98%) of **8** as a mixture of isomers (bp 73-85°C, 0.2 mmHg). IR (neat) 2207 cm^{-1} (CN). NMR data of the major isomer [2,3,4,5-tetramethyl-cyclopent-2-en-ylidene]-acetonitrile **8**: ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 4.88 (d, $^4J_{HH}$ = 1.7 Hz, 1H, =CH), 2.61 (br. q, $^3J_{HH}$ = 6 Hz, 1H, C*H*Me), 2.13 (br. q, $^3J_{HH}$ = 6 Hz, 1H, C*H*Me), 1.82 and 1.65 (br. s, 3H each, =C*Me*), 1.26 and 1.05 (d, $^3J_{HH}$ = 6 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 75 MHz, 25°C) δ 174.4 (*C*=CH), 155.4 (=*C*MeC=), 128.6 (*C*Me=CMe), 116.5 (*C*N),

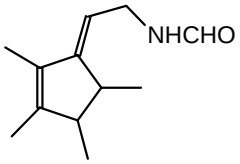
79.3 (=*C*H), 49.2 and 42.47 (CH), 16.2, 11.4, 10.4 and 7.2 (Me). Exact MS calcd. for $C_{11}H_{15}N$: 161.120, observed 161.120.

Synthesis of 2-[2,3,4,5-Tetramethyl-cyclopent-2-enylidene]-ethylamine (9).



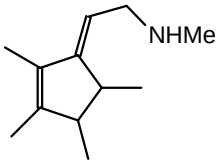
A solution of **8** (15.68 g, 97 mmol) in diethyl ether (50 mL) was slowly added to a suspension of $LiAlH_4$ (6 g, 0.15 mol) in 200 mL of diethyl ether. The mixture was refluxed for 3 h, after which water (15 mL) was slowly added. After 19 h, Na_2SO_4 (50 g) was added. The salts were filtered off and washed with 5 portions of diethyl ether (100 mL each). The combined filtrates were concentrated and the residue was distilled to give 11.19 g (68.5 mmol, 70%) of **9** as a mixture of isomers (bp 56 – 65°C, 0.03 mmHg). NMR data of the major isomer (with exocyclic double bond): ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 5.15 (t, $^3J_{HH}$ = 7.0 Hz, 1H, =CH), 3.38 (d, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2), 2.30 (br. q, $^3J_{HH}$ = 6 Hz, 1H, C*H*Me), 2.04 (br. m, 1H, C*H*Me), 1.66 and 1.58 (br. s, 3H each, =CMe), 1.02 and 0.97 (d, $^3J_{HH}$ = 7.0 Hz, 3H each, CH*Me*), N*H* not observed. ^{13}C(APT) NMR ($CDCl_3$, 75 MHz, 25°C) δ 150.6 (*C*=CH), 141.9 (=*C*MeC=), 127.9 (*C*Me=CMe), 114.3 (=CH), 48.7 (*C*HMe), 37.9 (NCH_2), 39.5 (*C*HMe), 19.3, 16.7, 10.5 and 7.6 (Me).

Synthesis of *N*-{2-[2,3,4,5-Tetramethyl-cyclopent-2-enylidene]-ethyl}-formamide (10).

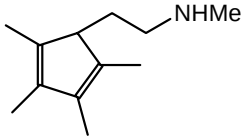


A mixture of **9** (11.8 g, 68 mmol) and ethyl formate (40 mL) was refluxed for 6 h. Excess formate and evolved ethanol were distilled off (70°C bath temperature, 19 mmHg) to give 13.3 g of crude **10** as a red oil. This was used without further purification for the synthesis of the methylamine derivative **7c**. IR (neat) 3293 (NH), 1665 (amide I), 1532 (amide II) cm^{-1}. NMR data of the major isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ 8.12 (s, 1H, C(O)H), 5.8 (br, 1H, NH), 4.99 (t, $^3J_{HH}$ = 7.0 Hz, 1H, =CH), 3.95 (m, 2H, NCH_2), 2.31 and 1.98 (br. q, $^3J_{HH}$ = 6 Hz, 1H each, C*H*Me), 1.64 and 1.53 (br. s, 3H each, =CMe), 0.95 and 0.90 (d, $^3J_{HH}$ = 6 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 75 MHz, 25°C) δ 161.97 (N*C*(O)H), 154.20 (*C*=CH), 143.81 (=*C*MeC=), 127.6 (*C*Me=CMe), 107.2 (=CH), 48.8 and 39.5 (*C*HMe), 34.4 (NCH_2), 19.2, 16.7, 10.6 and 7.6 (Me). Exact MS calcd. for $C_{12}H_{19}NO$: 193.147, observed 193.148.

Synthesis of *N*-Methyl-*N*-(2-(2,3,4,5-tetramethylcyclopentadienyl)ethyl)amine (7c).



A solution of crude **10** (13.3 g) in diethyl ether (50 mL) was slowly added to a suspension of $LiAlH_4$ (4.7 g, 123 mmol) in 200 mL of diethyl ether. The mixture was refluxed for 4 h, and then water (10 mL) was slowly added. After 19 h, 30 g of Na_2SO_4 was added, the salts were filtered off and washed with 5 portions of diethyl ether (100 mL each). The filtrates were concentrated and the residue distilled to give 11.1 g (62.3 mmol, 91% based on the amount of **9** used in the above preparation of **10**) of the methylamine derivative **7c** as a mixture of isomers, the major isomer having an exocyclic double bond (bp 46 – 50°C, 0.03 mmHg). IR (neat) 3295 (NH), 1645, 1532 (C=C) cm^{-1}. NMR data of the major isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 5.07 (d, $^3J_{HH}$ = 6.4 Hz, 1H, =CH), 3.20 (m, 2H, NCH_2), 2.35 (s, 3H, NMe), 2.30 and 1.95 (br. q, 1H each, C*H*Me), 1.62 and 1.53 (s, 3H each, =CMe), 0.92 and 0.88 (d, $^3J_{HH}$ = 6 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 75 MHz, 25°C) δ 151.8 (*C*=CH), 141.8 (=*C*MeC=), 128.0 (*C*Me=CMe), 111.3 (=CH), 49.0 (*C*HMe), 47.5 (NCH_2), 39.6 (*C*HMe), 33.6 (NCH_3), 19.2, 16.7, 10.5 and 7.6 (Me). Exact MS calcd. for $C_{12}H_{21}N$: 179.167, observed: 179.167.

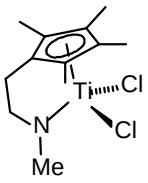


A portion of 5 g of the product as obtained above was isomerised by warming at 50°C in 10% aqueous HCl followed by addition of base, extraction into diethyl ether and Kugelrohr distillation (130°C, 0.5 mm Hg) to give 4 g (80% yield) of a mixture of isomers of **7c** with exclusively endocylic double bonds. ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ 2.70 – 2.40 and 2.25 – 2.0 (CH_2, C*H*Me), 2.30 – 2.20 (N*Me*), 1.85 – 1.60 (=C*Me*), 1.0 – 0.95 (CH*Me*).

Synthesis of $[C_5Me_4(CH_2)_2NR]Li_2$ (R = ^{t}Bu, 19a; ^{i}Pr, 19b; Me, 19c).

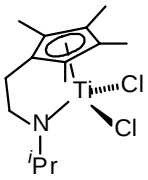
The dilithium salts of the cyclopentadienyl-amide ligands were prepared by reaction of $HC_5Me_4(CH_2)_2NHR$ with two equiv of ^{n}BuLi (hexane solution) in diethyl ether solvent at ambient temperature as described for the R = ^{t}Bu derivative in literature.[1c] The precipitates formed after stirring for 4 days were filtered off and rinsed repeatedly with pentane. These were dried *in vacuo* and used as such without further characterisation (NMR spectra in THF-d_8 were poorly resolved).

Synthesis of $[C_5Me_4(CH_2)_2NMe]TiCl_2$ (3c).



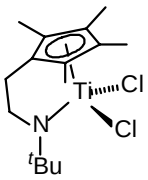
A mixture of $TiCl_3(THF)_3$ (1.16 g, 3.13 mmol) and $[C_5Me_4(CH_2)_2NMe]Li_2$ (**19c**, 0.85 g, 4.45 mmol; $[C_5Me_4(CH_2)_2NMe]Li_2$ is derived from **7c** that was previously isomerised to a mixture of isomers with exclusively endocyclic double bonds) were dissolved in 25 mL of THF and stirred at ambient temperature for 1 h and $PbCl_2$ (1.06 g, 3.81 mmol) was subsequently added to the resulting dark green solution. The resulting orange-brown suspension was stirred for one more hour, after which the solvent was pumped off. The residue was freed from residual solvents by stirring it with 2 portions of 10 mL pentane, which were subsequently removed *in vacuo*. The residue was subsequently extracted with pentane after which the solvent was removed *in vacuo*. Recrystallisation from 10 mL of toluene at –60°C yielded 0.36 g (1.21 mmol, 39%) of orange crystalline **3c**. ^{1}H NMR (300 Mhz, C_6D_6, 25°C) δ 3.89 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 3.37 (s, 3H, NMe), 2.67 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CCH_2), 1.97 and 1.83 (s, 6H each, Cp Me). ^{13}C(APT) NMR (75 MHz, C_6D_6, 25°C) δ 139.7, 129.4 and 125.7 (Cp C), 79.5 (NCH_2), 45.7 (NMe), 24.4 (CCH_2), 12.8 and 12.6 (Cp Me). Anal. calcd. for $C_{12}H_{19}NTiCl_2$: C, 48.68; H, 6.47; N, 4.73; Ti, 16.18. Found: C, 49.03; H, 6.36; N, 4.69; Ti, 16.01.

Synthesis of $[C_5Me_4(CH_2)_2N^iPr]TiCl_2$ (3b).



The R = ^{i}Pr derivative **3b** was prepared on 6.9 mmol scale according to the procedure described for R = Me (**3c**). The product mixture was extracted with 25 mL of pentane. Concentration and cooling of the extract to –25°C yielded 1.44 g (4.44 mmol, 60%) of analytically pure **3b** as an orange microcrystalline solid. ^{1}H NMR (300 MHz, C_6D_6, 25°C) δ 5.53 (sp, $^3J_{HH}$ = 6.2 Hz, 1H, ^{i}Pr CH), 3.94 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 2.68 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CCH_2), 2.01 and 1.84 (s, 6H each, Cp Me), 0.91 (d, $^3J_{HH}$ = 6.2 Hz, 6H, ^{i}Pr Me). ^{13}C(APT) NMR (75 MHz, C_6D_6, 25°C) δ 139.6, 128.7 and 125.8 (Cp C), 67.7 (NCH_2), 52.1 (NCH), 24.6 (CCH_2), 17.9 (^{i}Pr Me), 12.8 and 12.6 (Cp Me). Anal. calcd for $C_{14}H_{23}NTiCl_2$: C, 51.88; H, 7.15; N, 4.32; Ti, 14.78. Found: C, 51.85; H, 7.13; N, 4.27; Ti, 14.66.

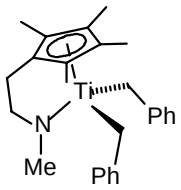
Synthesis of $[C_5Me_4(CH_2)_2N^tBu]TiCl_2$ (3a).



The R = ^{t}Bu derivative **3a** was prepared on 5.9 mmol scale according to the procedure described for R = Me (**3c**). Yield 0.65 g (1.92 mmol, 33%). ^{1}H NMR (300 MHz, C_6D_6, 25°C) δ 4.04 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 2.62 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CCH_2), 2.02 and 1.91 (s, 6H each, Cp Me), 1.41 (s, 9H, ^{t}Bu). ^{13}C(APT) NMR (75 MHz, C_6D_6, 25°C) δ 138.1,

129.4 and 128.6 (Cp C), 69.5 (NCH_2), 63.0 ($NCMe_3$), 29.0 (CMe_3), 25.3 (CCH_2), 13.4 and 12.8 (Cp Me). Anal. calcd. for $C_{15}H_{25}NTiCl_2$: C, 53.28; H, 7.45; N, 4.14; Ti, 14.16. Found: C, 53.03; H, 7.36; N, 4.02; Ti, 14.03.

Preparation of $[C_5Me_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (11c).



Two equivalents of $PhCH_2MgBr$ (2.15 M in diethyl ether, 0.4 mL, 0.86 mmol) were added to a solution of **3c** (111 mg, 375 μmol) in 19 mL of diethyl ether. The dark-red solution was stirred for 4 hours and the solvents were removed *in vacuo*. The residue was stripped of residual volatiles by stirring with 3 portions of 5 mL pentane, which were subsequently pumped off. The residue was extracted with 4 portions of 10 mL pentane. The solids were filtered off and the mixture was allowed to crystallise at –60°C. The solvent was decanted and removed *in vacuo*. Yield: 138 mg (0.34 mmol, 90%) of **11c**. ^{1}H NMR (300 MHz, C_6D_5Br, RT) δ 7.37 – 7.32 (m, 4H, PhH_o), 7.08 – 6.98 (m, 6H, Ph$H_{m,p}$), 3.92 (t, 2H, $^3J_{HH}$ = 7.2 Hz, NCH_2), 3.22 (s, 3H, NCH_3), 2.76 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CpCH_2), 2.17 (s, 6H, CpCH_3), 2.16 (s, 4H, PhCH_2), 1.78 (s, 6H, CpCH_3). ^{13}C(APT) NMR (75 MHz, C_6D_5Br, RT) δ 147.7 (PhC_{ipso}), 134.5 (CpC_{ipso}), 125.8 (m-Ph*C*), 124.0 (o-Ph*C*), 118.9 (p-Ph*C*), 116.5 (Cp*C*), 73.5 (*C*H_2Ph), 71.9 (N*C*H_2), 42.3 (N*C*H_3), 22.0 (Cp*C*H_2), 9.2 (Cp*C*H_3).

Reaction of 11c with $B(C_6F_5)_3$.

$B(C_6F_5)_3$ (26.0 mg, 50.1 mmol) was added to a solution of 20.1 mg **11c** in 0.5 mL C_6D_5Br. ^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 7.22 – 6.85 (m, 8H, Ph*H*), 6.18 (br. d, *J* = 7.3 Hz, 2H, Ph*H*), 3.73 (t, $^3J_{H,H}$ = 6.6 Hz, NCH_2), 3.34 (br. s, 3H, NCH_3), 2.67 (t, 2H, $^3J_{H,H}$ = 6.6 Hz, CpCH_2), 2.32 (br.s, 2H, BCH_2), 2.30 (br. s, 3H, CpCH_3), 1.71 (br. s, 6H, CpCH_3), 1.70 (br.s, 3H, $CpCH_3$), 1.60 (m, 2H, PhCH_2). ^{19}F NMR (188.15 MHz, C_6D_5Br, RT) δ –131.2 (d, $^3J_{FF}$ = 22.5 Hz, *o*-C_6F_5), –164.5 (t, $^3J_{FF}$ = 21.4 Hz, *p*-C_6F_5), –167.2 (t, $^3J_{FF}$ = 20.3 Hz, *m*-C_6F_5), $\Delta\delta(F_p–F_m)$ = 2.8 ppm. Upon addition of 1-hexene, heat was evolved indicating an exothermic reaction; ^{1}H NMR shows complete conversion to poly(1-hexene).

Attempted preparation of $[C_5Me_4(CH_2)_2N^iPr]Ti(CH_2Ph)_2$ (11b).

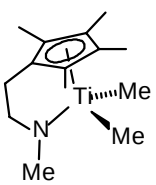
A solution of **3b** (141 mg, 0.44 mmol) in diethyl ether (20 mL) was cooled down to –80°C and 1 equivalent of $PhCH_2MgBr$ (0.96 M in diethyl ether, 0.45 mL, 0.44 mmol) was added. The mixture was allowed to warm up to room temperature and subsequently stirred for 2 hours. The solvents were removed *in vacuo* and the mixture was stripped of residual volatiles by stirring with 3 portions of 5 mL pentane, which were subsequently pumped of. An extraction with 6 portions of 15 mL pentane was carried out. The solvents were removed *in vacuo* and 19 mL of diethyl ether was added. One equivalent

of $PhCH_2MgBr$ (0.96 M in diethyl ether, 0.45 mL, 0.44 mmol) was added and the mixture was stirred for 2 hours. The solvents were removed *in vacuo* and the residue was stripped of residual volatiles by stirring with 3 portions of 5 mL pentane, which were subsequently pumped off. The residue was extracted with 2 portions of 20 mL pentane. Yield: 138 mg of a mixture of the mono– (**12b**) and di-benzyl (**11b**) compounds (indicated as A and B in the description of the ^{1}H NMR spectra, respectively). ^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 7.29 – 7.16 and 6.96 – 6.91 (m, 10 × PhH_A, 5 × PhH_B), 5.40 (sp, $^3J_{HH}$ = 6.3 Hz, 1H, ^{i}PrCH_A), 5.35 (sp, $^3J_{HH}$ = 6.3 Hz, 1H, ^{i}PrCH_B), 3.8-3.6 and 2.6-2.4 (2 × m, 4 × CpC$H_{2,A,B}$ & 4 × NC$H_{2,A,B}$), 2.21 (d, $^2J_{HH}$ = 10.7 Hz, 2H, Ti-$CH_{2,B}$), 2.15 (s, CpC$H_{3,A}$), 2.08 (d, $^2J_{HH}$ = 10.3 Hz, 1H, Ti$CH_{2,B}$), 2.00 (d, $^2J_{HH}$ = 10.7 Hz, 2H, Ti$CH_{2,B}$), 1.99 (d, $^2J_{HH}$ = 10.3 Hz, 1H, Ti$CH_{2,B}$), 1.81 (s, 3H, CpC$H_{3,B}$), 1.80 (s, 3H, CpC$H_{3,A}$), 1.74 (s, 3H, CpC$H_{3,A}$), 1.67 (s, 3H, CpC$H_{3,C}$), 1.64 (s, 3H, CpC$H_{3,B}$), 1.02 (d, $^3J_{HH}$ = 6.23 Hz, 3H, ^{i}PrC$H_{3,A}$), 0.82 (d, $^3J_{HH}$ = 6.41 Hz, 6H, ^{i}PrC$H_{3,B}$), 0.64 (d, $^3J_{HH}$ = 6.23 Hz, 3H, ^{i}PrC$H_{3,A}$).

Attempted preparation of [$C_5Me_4(CH_2)_2N^iPr$]Ti(CH_2Ph)(Me) (13b).

One equivalent of $PhCH_2MgBr$ (0.96 M in diethyl ether, 0.52 mL, 497 μmol) was added to a solution of **6b** (161 mg, 497 μmol) in 19 mL diethyl ether and the mixture was stirred for 1.5 hours. One equivalent of MeLi (1.4 M in diethyl ether, 0.36 mL, 497 μmol) was added at –80°C and the mixture was stirred for 1 hour at –80°C. The mixture was allowed to warm up to 0 °C and stirred for 1 hour at 0°C. The solvents were removed *in vacuo* at 0°C and the residue was stripped of residual volatiles by stirring with 4 portions of 5 mL pentane, which were subsequently pumped off. The residue was extracted with 3 portions of 20 mL pentane at 0°C. After evaporation of the solvent, compound **13b** was obtained as an orange oil as a mixture of the product and some side-products (mainly **14b**, approximately 5%, *vide infra*). ^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 7.25 – 6.94 (m, 5H, Ph*H*), 5.39 (sp, 1H, $^3J_{HH}$ = 6.6 Hz, ^{i}PrC*H*), 3.80-3.66 (m, 2H, NCH_2), 2.57 – 2.45 (m, 2H, CpCH_2), 2.00 (s, 3H, CpCH_3), 1.89 (s, 3H, CpCH_3), 1.72 (s, 3H, CpCH_3), 1.66 (s, 3H, CpCH_3), 1.14 (s, 1H, CH_2Ph), 1.12 (s, 1H, CH_2Ph), 0.94 (d, 3H, $^3J_{H,H}$ = 6.6 Hz, ^{i}PrCH_3), 0.90 (d, 3H, $^3J_{H,H}$ = 6.6 Hz, ^{i}PrCH_3), 0.31 (s, 3H, CH_3).

Preparation of [$C_5Me_4(CH_2)_2NMe$]$TiMe_2$ (14c).



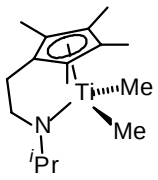
The reaction was performed in the absence of light.[43] Compound **3c** (192 mg, 0.65 mmol) was dissolved in diethyl ether (30 mL) and cooled to –80°C. MeLi (1.4 M in diethyl ether, 0.95 mL, 1.33 mmol) was added and the mixture was allowed to warm up to –20°C in 2.5 hours. The mixture was stirred at 0°C for 1 hour and the solvents were removed *in vacuo*. The residue was stripped of residual volatiles by stirring with

3 portions of 5 mL pentane, which were subsequently pumped off. The residue was extracted with 4 portions of 15 mL pentane. The mixture was transferred to a in a new Schlenktube and the solids were filtered off. Subsequently the volume was reduced and the mixture was allowed to crystallise at –80°C. The solvents were decanted and the orange crystals dried *in vacuo*. Yield: 50 mg (0.20 mmol, 30%) of **14c**. ^{1}H NMR (300 MHz, C_6D_6, RT) δ 3.79 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, NCH_2), 3.60 (s, 3H, NCH_3), 2.57 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, CpCH_2), 2.00 (s, 6H, CpCH_3), 1.73 (s, 6H, CpCH_3), 0.32 (s, 6H, TiCH_3). ^{13}C(APT) NMR (75 MHz, C_6D_6, RT) δ 121.7 (Cp*C*), 73.4 (N*C*H$_2$), 45.7 (Ti*C*H$_3$), 41.9 (N*C*H$_3$), 24.4 (Cp*C*H$_2$), 11.7 (2 × Cp*C*H$_3$).

Reaction of 14c with B(C_6F_5)$_3$.

^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 4.10 (t, $^{3}J_{H,H}$ = 7.1 Hz, 2H, NCH_2), 3.52 (s, 3H, NCH$_3$), 2.87 (t, $^{3}J_{H,H}$ = 7.1 Hz, 2H, CpCH_2), 1.89 (s, 6H, CpCH$_3$), 1.74 (s, 6H, CpCH$_3$), 0.80 (s, 6H, TiCH$_3$). ^{19}F NMR (188.15 MHz, C_6D_5Br, RT) δ –133.91 (d, $^{3}J_{FF}$ = 16.9 Hz, *o*-C_6F_5), –160.75 (t, *p*-C_6F_5), –165.08 (t, *m*-C_6F_5), Δδ(F_p–F_m) = 4.33 ppm. Upon addition of 1-hexene the reaction mixture warmed up (exothermic reaction); ^{1}H NMR shows complete conversion to poly(1-hexene).

Preparation of [$C_5Me_4(CH_2)_2N^iPr$]$TiMe_2$ (14b).



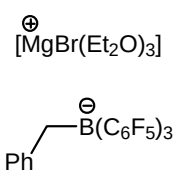
The reaction was performed in the absence of light. Compound **3b** (294 mg, 948 μmol) was suspended in diethyl ether (20 mL) and cooled down to –80°C. MeLi (1.4 M in diethyl ether, 1.4 mL, 1.89 mmol) was added while stirring. The mixture was allowed to warm up to 0°C and was stirred for 1 hour. The solvents were removed *in vacuo* at 0°C and the residue was stripped of residual volatiles by stirring with 2 portions of 5 mL pentane, which were subsequently pumped off. The residue was extracted with 3 portions of 19 mL pentane. The volume was reduced and the mixture was allowed to crystallise at –80°C. The solvents were decanted and the crystals dried *in vacuo*. Yield: 93 mg (0.33 mmol, 35%) of **14b**. ^{1}H NMR (300 MHz, C_6D_6, RT) δ 5.86 (sept, 1H, $^{3}J_{HH}$ = 6.6 Hz, ^{i}PrC*H*), 3.78 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2), 2.55 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2), 2.02 (s, 6H, CpCH_3), 1.73 (s, 6H, CpCH_3), 1.13 (d, 6H, $^{3}J_{HH}$ = 6.6 Hz, ^{i}PrCH_3), 0.24 (s, 6H, TiCH_3). ^{13}C(APT) NMR (75 MHz, C_6D_6, RT) δ 132.2 (Cp*C*), 123.8 (Cp*C*), 117.92 (Cp*C*), 60.9 (N*C*H$_2$), 48.7 (N*C*HMe$_2$), 43.6 (Ti*C*H$_3$), 24.6 (Cp*C*H$_2$), 20.3 (CH(*C*H$_3$)$_2$), 11.8 (Cp*C*H$_3$), 11.6 (Cp*C*H$_3$). Anal. Calcd. for $C_{16}H_{29}NTi$: C, 67.87; H, 10.25; N, 4.95; Ti, 16.93. Found: C, 67.84; H, 10.71; N, 4.92; Ti, 16.84.

Reaction of 14b with B(C_6F_5)$_3$.

^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 5.55 (br. sept, 1H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}PrC*H*), 4.09 (br. t, 2H, $^{3}J_{HH}$ = 7.3 Hz, CH_2), 2.99 – 2.72 (br., m, 2H, CH_2), 2.06 (br. s, 6H, CpCH_3), 1.72

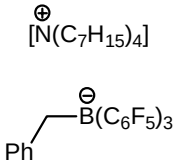
(br. s, 9H, CpCH_3), 0.99 (br. s, 6H, ^{i}PrCH_3), 0.78 (br. s, 6H, CH_3). ^{19}F NMR (188.15 MHz, C_6D_5Br, RT) δ –133.67 (d, *o*-C_6F_5), –160.11 (t, *p*-C_6F_5), –164.87 (t, *m*-C_6F_5), $\Delta\delta(F_p–F_m)$ = 4.76 ppm. Upon addition of 1-hexene the reaction mixture warmed up (exothermic reaction); ^{1}H NMR shows complete conversion to poly(1-hexene).

Synthesis of $[MgBr(Et_2O)_3][PhCH_2B(C_6F_5)_3]$ (16).



A solution of $PhCH_2MgBr$ (2.0 mL, 0.95 M in diethyl ether, 1.95 mmol) was added to a solution of $B(C_6F_5)_3$ (1.000 g, 1.9 mmol) in 40 mL of diethyl ether and the resulting solution was stirred for two hours. The solution was concentrated to 19 mL, upon which a white precipitate formed. The precipitate was isolated and washed with three portions of diethyl ether (10 mL each), and dried *in vacuo* resulting in 1.032 g. (1.11 mmol, 57%) of **16**. ^{1}H NMR (500 MHz, CD_2Cl_2, RT) δ 6.88 (ps. t, *J* = 7.3 Hz, 2H, Ph), 6.79 (ps. t, *J* = 7.3 Hz, 1H, Ph), 6.74 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 4.01 (q, $^3J_{HH}$ = 6.8 Hz, OCH_2, 12H), 3.01 (s, broad, $\Delta\nu_{½}$ = 12.3 Hz, 2H, BCH_2), 1.55 (t, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3, 18H). ^{13}C{^{1}H} NMR (125.9 MHz, CD_2Cl_2, RT) δ 148.9 (*ipso*-Ph), 148.5 (d, $^1J_{CF}$ = 237.3 Hz, *o*-C_6F_5), 137.8 (d, $^1J_{CF}$ = 241.10 Hz, *p*-C_6F_5), 136.7 (d, $^1J_{CF}$ = 245.67 Hz, *m*-C_6F_5), 128.9 (Ph), 127.1 (Ph), 122.7 (Ph), 68.1 (OCH_2CH_3), 31.9 (b, $\Delta\nu_{½}$ = 120 Hz, B-CH_2), 14.2 (OCH_2CH_3). C_6F_5 *ipso*-C not observed. ^{19}F NMR (188.15 MHz, CD_2Cl_2, RT) δ –132.6 (d, $^3J_{FF}$ = 27.2 Hz, 2F, *o*-C_6F_5), –166.0 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –168.8 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *m*-C_6F_5) ($\Delta\delta(F_p–F_m)$ = 2.8 ppm).

Synthesis of tetraheptylammonium benzyltrispentafluorophenylborate (17).



A solution of 219 mg (0.401 mmol) of tetraheptylammoniumchloride was added to a solution of 405 mg **16** (0.403 mmol) in 19 mL of dichloromethane, resulting in a white suspension. The solution was filtered over Celite and the precipitate washed with dichloromethane. The solvents were removed from the combined filtrates *in vacuo*, resulting in (207 mg, 0.205 mmol, 51%) of a colourless oil (**17**). ^{1}H NMR (500 MHz, toluene-d_8, RT) δ 7.1 – 6.9 (m, Ph, overlapping with residual solvent peaks), 6.82 (t, $^3J_{HH}$ = 7.32 Hz, 1H), 3.24 (broad, $\Delta\nu_{½}$ = 9.5 Hz, 2H, BCH_2), 3.39 (broad, $\Delta\nu_{½}$ = 21.2 Hz, 8H, NCH_2), 1.30 (p, $^3J_{HH}$ = 6.8 Hz, 8H), 1.20 (m, 16H), 1.08 (m, 16H), 0.95 (t, $^3J_{HH}$ = 7.3 Hz, 12H). ^{13}C{^{1}H} NMR (125.7 MHz, toluene-d_8, RT) δ 149.0 (d, $^1J_{CF}$ = 239.6 Hz, *o*-C_6F_5), 148.7 (*ipso*-Ph), 138.2 (d, $^1J_{CF}$ = 244.9 Hz, *p*-C_6F_5), 137.1 (d, $^1J_{CF}$ = 245.7 Hz, *m*-C_6F_5), 129.1 (Ph), 127.6 (Ph), 123.5 (Ph), 58.6 (NCH_2), 32.7 (b, $\Delta\nu_{½}$ = 108 Hz, BCH_2), 31.8, 29.0, 26.3, 22.9, 21.7 (heptyl-CH_2's), 14.1 (heptyl-CH_3). C_6F_5 *ipso*-C not observed. ^{19}F NMR (188.15 MHz, toluene-d_8, RT) δ –131.5 (d, $^3J_{FF}$ = 29.4 Hz, 2F, *o*-C_6F_5), –164.5 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –167.5 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *m*-C_6F_5), ($\Delta\delta(F_p–F_m)$ = 2.9 ppm). ^{1}H NMR (200 MHz, CD_2Cl_2, RT) δ 6.97 – 6.70 (m, 5H, Ph),

2.99 (br t, $^3J_{HH}$ = 8.0 Hz, 8H, NCH_2), 2.81 (br s, $\Delta\nu_{½}$ = 11.8 Hz, 2H, BCH_2), 1.69 – 1.25 (br m, 40H, CH_2), 0.89 (t, $^3J_{HH}$ = 6.40 Hz, 12H). ^{19}F NMR (188.15 MHz, CD_2Cl_2, RT) δ –132.4 (d, $^3J_{FF}$ = 23.7 Hz, 2F, *o*-C_6F_5), –165.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), –168.7 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *m*-C_6F_5) ($\Delta\delta(F_p–F_m)$ = 2.9 ppm). ^{1}H NMR (200 MHz, C_6D_5Br, RT) δ 7.09 – 6.80 (m, Ph, overlapping with residual solvent peaks), 3.22 (br s, $\Delta\nu_{½}$ = 13.8 Hz, 2H, BCH_2), 2.70 (br s, 28 Hz, 8H, NCH_2), 1.45 – 0.97 (m, 40H, CH_2), 0.97-0.78 (m, 12H, CH_3). ^{19}F NMR (188.15 MHz, toluene-d_8, RT) δ –131.4 (d, $^3J_{FF}$ = 23.7 Hz, 2F, *o*-C_6F_5), –164.4 (t, $^3J_{FF}$ = 20:3 Hz, 1F, *p*-C_6F_5), –167.2 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *m*-C_6F_5) ($\Delta\delta(F_p–F_m)$ = 2.9 ppm).

General considerations, polymerisation experiments.
Toluene (Aldrich anhydrous, 99.5%) was passed over supported Cu scavenger (BASF R3-11) and a 1:1 mixture of alumina (granules, 2-5 mm, Fluka) and molecular sieves (4Å) and stored under nitrogen in a vessel, directly connected to the autoclave setup. Ethene and propene (AGA, polymer grade) were passed over columns of supported Cu scavenger (BASF R3–11) and molecular sieves (4Å) before being passed to the reactor.
GPC was performed at 135°C on 1,2,4-trichlorobenzene solutions of the polymers with a Polymer Laboratories PL–GPC210 instrument. ^{13}C NMR spectra of the polypropenes were recorded at 75°C in 1,1,2,2-tetrachloroethane-d_2 (Aldrich, used as purchased) on a Varian Unity 500 spectrometer operating at 125.7 MHz. The ^{13}C NMR spectra were referenced to the resonances of the carbon atom in the deuterated solvent (δ 74.12 ppm).

Olefin polymerisation with dichloride/MAO systems.
Polymerisation experiments were carried out in a thermostated (electrical heating, water cooling) 1 L stainless steel autoclave (Medimex), equipped with solvent and catalyst injection systems. The autoclave was pre-dried by heating *in vacuo* at 120°C for 1 h. After cooling to the desired reaction temperature toluene solvent (200 mL) was injected. Propene or ethene (2 bar) was admitted and the mixture was allowed to equilibrate for 15 min. followed by the injection of 5 mL of a 1.5 M MAO/toluene solution. Polymerisation was initiated by injection of a solution of the appropriate titanium dichloride complex in 10 mL of toluene. The total amount of toluene in the reactor (including portions used to rinse the injector) was 250 mL. During the run the monomer pressure was kept constant within 0.1 bar by replenishing flow.
Ethene polymerisations: After the run the reactor was vented, opened to ambient and 10 mL of methanol was added to the reaction mixture. The polymer was collected on a frit and subsequently poured into acidified methanol and stirred for several hours. The polyethene was then collected on a frit, rinsed repeatedly with methanol and light petroleum ethers and dried *in vacuo* at 70°C.

Propene polymerisations: After the run the polymer solution was pressure flushed from the reactor and the reactor was rinsed with 2 portions of 100 mL warm (75°C) toluene. To the polymer solution 10 mL of methanol was added. The solvent was removed from the mixture *in vacuo*, the residue was dissolved in dichloromethane and the solution was filtered. The solvent was removed on a rotary evaporator at 70–80°C.

Olefin polymerisation with dialkyl/borane or dialkyl/borate systems.
Polymerisation experiments were carried out in a thermostated (electrical heating, water cooling) 500 mL stainless steel autoclave (Medimex), equipped with solvent and catalyst injection systems. The autoclave was pre-dried by heating *in vacuo* at 120°C for 1 h. After cooling to the desired reaction temperature toluene solvent (150 mL) was injected. Propene or ethene (2 bar) was admitted and the mixture was allowed to equilibrate. The activator was injected as a toluene solution (5 – 10 mL) and the flask and injector were rinsed with two portions of 5 – 10 mL of toluene. Polymerisation was initiated by injection of a solution of the appropriate titanium dialkyl complex in 10 mL of toluene followed by two rinsing portions of 5 – 10 mL toluene. The total amount of toluene in the reactor (including portions used to rinse the injector) was 200 mL. During the run the monomer pressure was kept constant within 0.1 bar by replenishing flow.
For the runs with the added anion **17** the reactor the procedure is identical as described above, but starting with 125 mL of toluene solvent, followed by injection of the activator (toluene solution, 5 – 10 mL), rinsing of the flask and injector with 2 portions of 5–10 mL of toluene, injection of 5 – 10 mL of a toluene solution of **17** and rinsing of the flask and injector with 2 portions of 5 – 10 mL of toluene. Polymerisation was initiated by injection of a solution of the appropriate titanium dialkyl complex in 10 mL of toluene followed by two rinsing portions of 5 – 10 mL toluene. The total amount of toluene in the reactor (including portions used to rinse the injector) was 200 mL. During the run the monomer pressure was kept constant within 0.1 bar by replenishing flow.
After the run the polymer solution was pressure flushed from the reactor and the reactor was rinsed with 2 portions of 100 mL warm toluene. The solvents were removed on a rotary evaporator at 70 – 80°C.

2.4 References

[1] (a) Canich, J.M. US 5026798, 1991 issued to Exxon; (b) Canich, J.M. EP 426436, 1991 issued to Exxon; (c) Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S.-Y. EP 416815, 1991 issued to Dow; (d) Stevens, J.C.; Neithamer, D.R. EP 418022, 1991 issued to Dow; (e) Canich, J.A.M. US 5504169, 1996 issued to Exxon.

[2] For an overview of the research in this area, see: McKnight, A. L.; Waymouth, R. M. *Chem. Rev*. **1998**, *98*, 2587-2598.

[3] Stevens, J.C. *Stud. Surf. Sci. Catal.* **1996**, *101*, 11-20.

[4] Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143-1170 and references cited.

[5] (a) Shapiro, P.J.; Bunel, E.; Schaefer, W.P.; Bercaw, J.E. *Organometallics* **1990**, *9*, 867-869; (b) Piers, W.E.; Shapiro, P.J.; Bunel, E.; Bercaw, J.E. *Syn. Lett.* **1990**, 74-84; (c) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623-4640.

[6] (a) Burger, B.J.; Thompson, M.E.; Cotter, W.D.; Bercaw, J.E. *J. Am. Chem. Soc.* **1990**, *112*, 1566-1577; (b) Bunel, E.; Burger, B.J.; Bercaw, J.E. *J. Am. Chem. Soc.* **1988**, *110*, 976-978.

[7] Okuda, J. *Chem. Ber*. **1990**, *123*, 1649-1651.

[8] (a) Canich, J.A.M. EP 420436 A1, 1991, assigned to Exxon Chemical Patents Inc.; (b) Stevens, J.C.; Neithamer, D.R. EP 418044 A2, 1991 issued to the Dow Chemical Company; (c) Canich, J.A.M. US 5096867, 1992, assigned to Exxon Chemical Patents Inc.; (d) LaPointe, R.E.; Rosen, R.K.; Nickias, P.N. EP 495375 A2, 1992, assigned to the Dow Chemical Company; (e) LaPointe, R.E.; Stevens, J.C.; Nickias, P.N.; McAdon, M.H. EP 520732 A1, 1992, assigned to the Dow Chemical Company; (f) Brant, P.; Canich, J.A.M. WO 93/12151, 1993, assigned to Exxon Chemical Patents Inc.; (g) Lai, S.I.; Wilson, J.R.; Knight, G.W.; Stevens, J.C. WO 93/08221, 1993, assigned to the Dow Chemical Company; (h) Brant, P.; Canich, J.A.M.; Merrill, N.A. WO 93/21242, 1993, assigned to Exxon Chemical Patents Inc.; (i) Brant, P.; Canich, J.A.M.; Dias, A.J.; Bamberger, R.L.; Licciardi, G.F.; Henrichs, P.M. WO 94/07930, 1994, assigned to Exxon Chemical Patents Inc.; (j) Panell, R.B.;Canich, J.A.M.; Hlatky, G.G. WO 94/00500, 1994, assigned to Exxon Chemical Patents Inc.; (k) Rosen, R.K.; Nickias, P.N.; Devore, D.D.; Stevens, J.C.; Timmers, F.J.; US 5374696, 1994, assigned to the Dow Chemical Company; (l) Devore, D.D.; Crawford, L.H.; Stevens, J.C.;Timmers, F.J.; Mussell, R.D.; Wilson, D.R.; Rosen, R.K. WO 95/00526, 1995, assigned to the Dow Chemical Company; (m) Canich, J.A.M. WO 96/00244, 1996, assigned to Exxon Chemical Patents Inc.; (n) Nickias, P.N.; McAdon, M.H.; Patton, J.T. WO 97/15583, 1997, assigned to the Dow Chemical Company.

[9] (a) Martínez, S.; Exposito, M.T.; Ramos, J.; Cruz, V.; Martínez, M.C.; López, M.; Muñoz-Escalona, A.; Martínez-Salazar, J. *J. Pol. Sci. A: Pol. Chem.* **2005**, *43*, 711-725; (b) Walter, P.; Trinkle, S.; Suhm, J.; Mder, D.; Friedrich, C.; Mülhaupt, R. *Macromol. Chem. Phys.* **2000**, *201*, 604-612.

[10] (a) Santos, J.M.; Ribeiro, M.R.; Portela, M.F.; Cramail, H.; Deffieux, A. *Macromol Chem. Phys*. **2001**, *202*, 3043-3048; (b) Santos, J.M.; Ribeiro, M.R.; Portela, M.F.; Cramail, H.; Deffieux, A.; Antinolo, A.; Otero, A.; Prashar, S. *Macromol Chem. Phys.* **2002**, *203*, 139-145;

[11] (a) Harrington, B.A. WO 96/40806, 1996, assigned to Exxon Chemical Patents Inc.; (b) Harrington, B.A.; Hlatkey, G.G.; Canich, J.A.M.; Merrill, N.A. US 5635573, 1997, assigned to Exxon Chemical Patents Inc.

[12] (a) Thorshaug, K.; Mendichi, R.; Boggiono, L.; Tritto, I.; Trinkle, S.; Friedrich, C.; Mülhaupt *Macromolecules* **2002**, *35*, 2903-2911; (b) Lasarov, H.; Pakkanen, T.T. *Macromol. Rapid Commun.* **2001**, *22*, 434-438; (c) Harrington, B.A.; Crowther, D.J. *J. Mol. Catal. A: Chem.* **1998**, *128*, 79-84.

[13] Sinnema, P.-J., Ph.D. Thesis, *Carbon-Bridged Cyclopentadienyl Amido Group 4 Metal Complexes, Ligand tuning and Olefin Polymerization*, University of Groningen, Groningen 1999.

[14] Sinnema, P. J.; Hessen, B.; Teuben, J. H. *Macromol. Rapid. Commun.* **2000**, *21*, 562-566.

[15] Ypey, E.G.; Van Beek, J.A.; Gruter, G.J.M. WO 97/42157, 1997 assigned to DSM N.V.

[16] Krut'ko, D.P.; Borzov, M.V.; Veksler, E.N.; Kirsanov, R.S.; Churakov, A.V. *Eur. J. Inorg. Chem.* **1999**, 1973-1979.

[17] Jolly, P.W.; Döhring, A.; Weber, J.C. WO 01/02323, November 1, 2001 assigned to Studiengeselschaft Kohle mbH.

[18] (a) Kauffmann, T.; Ennen, J.; Lhotak, H.; Rensing, A.; Steinseifer, F.; Woltermann, A. *Angew. Chem.* **1980**, *92*(4), 321-323; (b) Kauffmann, T.; Berghus, K.; Rensing, A.; Ennen, J. *Chem. Ber*. **1985**, *118*, 3737-3747; (c) Kauffmann, T.; Berghus, K.; Rensing, A. *Chem. Ber*. **1985**, *118*, 4507-4516.

[19] (a) Okuda, J.; Zimmermann, K. H. *J. Organomet. Chem.* **1988**, *344*, C1-C4 (b) Bensley Jr, D. M.; Mintz, E. A.; Sussangkarn, S. J. *J. Org. Chem.* **1988**, *53*, 4417-4419; (c) Fendrick, C.; Schertz, L. D.; Mintz, E. A.; Marks, T. J. *Inorg. Synth.* **1992**, *29*, 193-197.

[20] For properties and stabilities of (functionalised) organolithium and Grignard reagents, see: (a) Wardell, J. (Ch. 2) and Lindsell, W.E. (Ch. 4) in *Comprehensive Organometallic Chemistry*; Wilkinson. G.; Stone, F.G.A.; Abel, E.W., Eds; Pergamon: Oxford, U.K., 1982; Vol. 1. (b) Wright, D.S.; Beswick, M.A. (Ch. 1) and Lindsell, W.E. in *Comprehensive Organometallic Chemistry II*; Abel, E.W.; Stone, F.G.A.; Wilkinson. G.; Housecroft, C.E. Eds; Pergamon: Oxford, U.K., 1995; Vol. 1.

[21] Wittig, G.; Reiff, H. *Angew. Chem.* **1968**, *80*, 8-15.

[22] Canich, J.A.M.; Licciardi, G.F. US 5057475, 1991 assigned to Exxon Chemical Patents Inc.

[23] Devore, D.D. EP 514828 A1, 1992 assigned to The Dow Chemical Company.

[24] (a) Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun*. **1990**, 1470-1471; (b) McKnight, A.L.; Masood, A.; Waymouth, R.M.; Straus, D.A. *Organometallics* **1997**, *16*, 2879-2885.

[25] (a) Talarico, G.; Busico, G.; Cavallo, L. *J. Am. Chem. Soc*. **2003**, *125*, 7172-7173; (b) Lambert, M.; Gliubizzi, R.; Mazzeo, M.; Tedesco, C.; Pellecchia, C. *Marcomolecules* **2004**, *37*, 276-282.

[26] Hawlerak, E.J.; Deck, P.A. *Organometallics* **2003**, *22*, 3558-3565.

[27] (a) Horton, A.D.; Dewith, J.; Vanderlinden, A.J.; Vandeweg, H. *Organometallics* **1996**, *15*, 2672-2674; (b) Horton, A.D. *Organometallics* **1996**, *15*, 2675-2677.

[28] Zemánek, J.; Štěpnička, P. Fejfarová, K.; Gyepes, R.; Císařová, I.; Horáček, M.; Kubišta, J.; Varga, V.; Mach, K. *Collect. Czech. Chem. Commun.*, **2001**, *66*, 605-620.

[29] Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572-1581.

[30] (a) Yang, X; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc*. **1991**, *113*, 3623-3625; (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015-10031.

[31] (a) Ewen, J.A.; Elder, M.J. EP 426638 A2, 1990 assigned to Fina Technology Inc.; (b) Ewen, J.A.; Elder, M.J., EP 427697, 1991 assigned to Fina Tachnology, Inc.; (c) Ewen, J.A.; Elder, M.J., US 5561092, 1996 assigned to Fina Technology, Inc.

[32] Chen, J.C.W.; Tsai, W.M.; Rausch, M.D. *J. Am. Chem. Soc.* **1991**, *113*, 8570-8571.

[33] The in the reaction liberated 1,1,1,2-tetraphenylethane is expected to not coordinate to the resulting ion pair.[34]

[34] Lancaster, S.J.; Bochmann, M. *J. Organomet. Chem.* **2002**, *654*, 221-223.

[35] The catalytic system is therefore very sensitive towards impurities and this sometimes hampers the production of good duplicate runs. It should be noted that the presented titanium concentration ([Ti]) is probably higher than the actual catalyst concentration, since the active catalyst in our case can be assumed to act in part as a scavenger. It is assumed that the products, formed by the reaction of the catalyst with impurities, are inactive in the polymerisation.

[36] (a) Lai, S.-Y.; Wilson, J.R.; Knight, G.W.; Stevens, J.C. WO 93/08221, 1993 assigned to the Dow Chemical Company; (b) Jacobsen, G.B.; Wijkens, P.; Jastrzebski, J.T.B. H.; Van Koten, G. US 5834393, 1998 issued to The Dow Chemical Company; (c) Hinokuma, S.; Miyake, S.; Ono, M.; Inazawa, S. US 5869723, 1999 issued to Showa Denko K.K..

[37] See e.g. Von Seidel, W.; Bürger, I. *Z. Anorg. Allg. Chem.* **1978**, *447*, 195-198.

[38] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135-140.
[39] Snyder, H.R.; Matteson, D.S. *J. Am. Chem. Soc.* **1957**, *79*, 2217-2221.
[40] Newcomb, M.; Varick, T.R., Goh, S.-H. *J. Am. Chem. Soc.* **1990**, *112*, 5186-5193.
[41] (a) Canich, J.M.; Hlatky, G.G.; Turner, H.W. WO 92/00333, 1992; Canich, J.M. EP 420436 A1, 1991, issued to Exxon Chemical Co.; (b) Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S. EP 416812 A2, 1990 issued to Dow Chemical Co.
[42] Pohlmann, J.L.W.; Brinckmann, F.E. *Z. Naturforschg.* **1965**, *20b*, 5-11.
[43] Hawlerak, E.J.; Deck, P.A. *Organometallics* **2003**, *22*, 3558-3565.